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Liquid Chromatography Electrospray Ionization Mass Spectrometric (LC-ESI-MS) and Desorption Electrospray Ionization Mass Spectrometric (DESI-MS) Identification of Chemical Warfare Agents in Consumer Products

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DRDC Suffield

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Abstract

Terrorist use of chemical warfare agents could involve contamination of consumer products with chemical warfare agents or other toxic chemicals. Liquid chromatography electrospray ionization mass spectrometry (LC-ESI-MS) and desorption electrospray ionization mass spectrometry (DESI-MS) have been used at DRDC Suffield for the identification of chemical warfare agents and both approaches were evaluated for the determination of chemical warfare agents in spiked consumer products. Three consumer products, bottled water, canola oil and corn meal, were selected as candidates for the evaluation and comparative purposes. Each of these media was contaminated with low μg/g levels of chemical warfare agents, levels typically used for evaluation purposes by the Organisation for the Prohibition of Chemical Weapons (OPCW). In house LC-ESI-MS and LC-ESI-MS/MS methods were evaluated for the determination of chemical warfare agents in spiked bottled water samples. The headspaces above spiked corn meal and canola oil samples were sampled with SPME fibers and the fibers were analysed by DESI-MS and DESI-MS/MS. MS data for all the spiked compounds were acquired in the continuum mode with a resolution of 8000, which typically resulted in mass measurement errors of 0.002 Da or less. Application of the developed sample handling and analysis methodologies is anticipated during forensic or other investigations where consumer products have been deliberately contaminated with chemical warfare agents.

Résumé

L'utilisation terroriste d'agents de guerre chimiques pourrait consister à contaminer des produits de consommation avec des agents de guerre chimiques ou autres produits chimiques toxiques. La méthode de spectrométrie de masse avec ionisation par électronébulisation et chromatographie en phase liquide (SM-ESI-CPL) et la méthode de spectrométrie de masse avec ionisation par électronébulisation et désorption (SM- DESI) ont été utilisées à DRDC Suffield pour identifier les agents de guerre chimiques et les deux méthodes ont été évaluées pour leur efficacité à déterminer la présence d'agents de guerre chimiques semés dans les produits de consommation. Trois produits de consommation, de l'eau embouteillée, de l'huile de colza et de la semoule de mais, ont été sélectionnés comme candidats à une évaluation et comparaison. On a contaminé chacun de ces milieux avec de faibles quantités μg/g d'agents de guerre chimiques, quantités normalement utilisées par l'Organisation pour l'interdiction des armes chimiques (OIAC) dans le but d'effectuer une évaluation. On a utilisé les méthodes internes d'évaluation SM-ESI-CPL et SM/SM-ESI-CPL pour évaluer l'efficacité à déterminer la présence d'agents de guerre chimiques dans des échantillons d'eau embouteillée. Les vides au-dessus des échantillons de semoule de mais et d'huile de soja ensemencés ont été échantillonnés avec des fibres SPME; ces fibres ont été analysés au moyen des méthodes SM-DESI et SM-DESI/SM. Les données de la SM obtenues pour tous les composés ensemencés ont été obtenues en mode continu avec une résolution de 8000 ce qui a généralement résulté en des erreurs de mesure de masse de 0,002 Da ou moins. On prévoit que les méthodologies d'analyse et de manipulation des échantillons, mis au point durant les investigations légistes ou autres, seront appliquées aux produits de consommation ayant été contaminés avec des agents de guerre chimiques.

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Executive summary

Introduction: A collaborative initiative involving DRDC Suffield, the Canadian Food Inspection Agency, ThermoFisher and the National Research Council was funded for the development and evaluation of high-field asymmetric waveform ion mobility mass spectrometry (FAIMS-MS) for the rapid separation and identification of chemical and biological warfare agents in food and consumer matrices (CRTI-04-0022RD). The first phase of three involves the assessment of FAIMS-MS for chemical warfare agent detection in consumer products. The developed methods were to be compared to liquid chromatography-mass spectrometry (LC-MS) and other MS techniques being used by DRDC Suffield, the National Laboratory for Chemical Warfare Agent Identification.

Results: Liquid chromatography electrospray ionization mass spectrometry (LC-ESI-MS) and desorption electrospray ionization mass spectrometry (DESI-MS) have been used at DRDC Suffield for the identification of chemical warfare agents in spiked samples and both approaches were evaluated for the determination of chemical warfare agents in spiked consumer products. Three consumer products, bottled water, canola oil and corn meal, were selected as candidates for the evaluation and comparative purposes. Each of these media were contaminated with low μg/g levels of chemical warfare agents, levels typically used for evaluation purposes by the Organisation for the Prohibition of Chemical Weapons (OPCW). LC-ESI-MS and LC-ESI-MS/MS methods were used to successfully identify chemical warfare agents in spiked bottled water samples. The headspace above spiked corn meal and canola oil samples were sampled with SPME fibers. Direct analysis of SPME fibers exposed to the headspace above spiked corn meal and canola oil samples by DESI-MS and DESI-MS/MS resulted in the identification of many of the spiked compounds. MS data for all the spiked compounds were acquired in the continuum mode with a resolution of 8000, which typically resulted in mass measurement errors of 0.002 Da or less.

Significance: Application of the developed sample handling and analysis methodology is anticipated during forensic or other investigations where evidence of chemical warfare agent use is required for criminal prosecution or to insure the safety of consumer products.

Future Plans: The reported methodologies will be a valuable addition to the in-house methods for the identification of chemical warfare agents and their hydrolysis products in samples collected in support of counter-terrorism. Continued development and application of tandem mass spectrometry to samples containing chemical warfare agents is anticipated at DRDC Suffield with a focus on rapid, DESI-MS/MS applications.

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Sommaire

Introduction: Une initiative collaborative entre RDDC Suffield, l'Agence canadienne d'inspection des aliments, ThermoFisher et National Research Council a été financée pour la mise au point et l'évaluation de la spectrométrie de masse de haute résolution de la mobilité des ions avec forme d'onde asymétrique (FAIMS-MS) pour la séparation et l'identification rapides des agents de guerre chimiques et biologiques contenus dans les matrices de nourriture et de produits de consommation courante (CRTI-04-0022RD). La première des trois phases consiste à évaluer la méthode FAIMS-MS pour la détection d'un agent de guerre chimique dans les produits de consommation. Les méthodes mises au point devaient être comparées à celle du couplage de chromatographie en phase liquide et spectrométrie de masse (CPL-SM) et autres techniques de SM utilisées par RDDC Suffield et le laboratoire national pour l'identification des agents de guerre chimique.

Résultats: La méthode de spectrométrie de masse avec ionisation par électronébulisation et chromatographie en phase liquide (SM-ESI-CPL) et la méthode de spectrométrie de masse avec ionisation par électronébulation et désorption (SM- DESI) ont été utilisées à DRDC Suffield pour identifier les agents de guerre chimiques dans des échantillons ensemencés et les deux méthodes ont été évaluées pour leur efficacité à déterminer la présence d'agents de guerre chimiques semés dans les produits de consommation. Trois produits de consommation, de l'eau embouteillée, de l'huile de colza et de la semoule de mais, ont été sélectionnés comme candidats à une évaluation et comparaison. On a contaminé chacun de ces médias avec de faibles quantités µg/g d'agents de guerre chimiques, quantités normalement utilisées par l'Organisation pour l'interdiction des armes chimiques (OIAC) dans le but d'effectuer une évaluation. On a utilisé les méthodes internes d'évaluation SM-ESI-CPL et SM/SM-ESI-CPL pour évaluer l'efficacité à déterminer la présence d'agents de guerre chimiques dans des échantillons d'eau embouteillée. Les vides au-dessus des échantillons de semoule de mais et d'huile de soja ensemencés ont été échantillonnés avec des fibres SPME. L'analyse directe des fibres SPME ayant été exposés dans le vide au-dessus des échantillons de la semoule de mais et l'huile de soja par les méthodes SM- DESI et SM-DESI/SM ont résulté en l'identification de plusieurs composés ensemencés. Les données de la SM pour tous les composés ensemencés ont été acquis en mode continu avec une résolution de 8000 ce qui ce qui a généralement résulté en des erreurs de mesure de masse de 0,002 Da ou moins.

La portée des résultats: On prévoit que des méthodologies d'analyse et de manipulation des échantillons mis au point seront appliquées durant les investigations légistes ou autres où il faut prouver, en vue d'une poursuite criminelle ou pour assurer la sécurité des produits de consommation, qu'un agent de guerre chimique a été utilisé.

Plans futurs: Les méthodologies documentées seront un ajout important aux méthodes internes d'indentification des agents de guerre chimiques et de leurs produits d'hydrolyse dans les échantillons recueillis en soutien à l'antiterrorisme. On prévoit que RDDC Suffield continuera la mise au point e l'application de la spectrométrie de masse en tandem aux échantillons contenant des agents de guerre chimiques en focalisant sur les applications rapides de SM-DESI/SM.

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Introduction

The ending of the Cold War and the widespread acceptance of the Chemical Weapons Convention has reduced the likelihood of battlefield chemical weapons use, but there remains serious concern world-wide that other parties may use chemical warfare agents against civilian or military targets. Within Canada, one of the initiatives to counter terrorism was the establishment of the Chemical, biological, radiological and nuclear Research and Technology Initiative (CRTI). This research-oriented organization originally formed three clusters to deal with the challenges associated with each of chemical, biological and nuclear use. Two years ago CRTI raised concern about possible contamination of consumer products with toxic chemicals including chemical warfare agents and invited R&D proposals that addressed the rapid detection and identification of these compounds in candidate media.

A collaborative initiative involving DRDC Suffield, the Canadian Food Inspection Agency, ThermoFisher and the National Research Council was funded for the development and evaluation of high-field asymmetric waveform ion mobility mass spectrometry (FAIMS-MS) for the rapid separation and identification of chemical and biological warfare agents in food and consumer matrices (CRTI-04-0022RD). The first phase of three involves the assessment of FAIMS-MS for chemical warfare agent detection in consumer products. The developed methods were to be compared to liquid chromatography electrospray ionization mass spectrometry (LC-ESI-MS) and other MS techniques being used by DRDC Suffield, the National Laboratory for CW Agent Identification.

The development of analytical methods for the detection and identification of chemical warfare agents, their degradation products and related compounds has been thoroughly reviewed with different emphases on a number of occasions (1-9). Much of the analytical methods development was driven by the requirements of the military and their need to be able to detect and identify these compounds in typical battlefield samples. These methods focused largely on the determination of chemical warfare agents or their degradation products in environmental matrices such as soil (10-18), water (17, 19-22), air (23, 24), recovered munitions and munition blocks (12, 13, 25), decontamination solutions (26-28) and military clothing/gear (10, 12, 13). Newer methods based on solid phase microextraction (SPME) sampling followed by GC-MS analysis (29-34) and direct analysis by secondary ion mass spectrometry (35, 36) have been reported for environmental analyses, but most of the reported analytical methods are based on gas chromatography mass spectrometry (GC-MS) analysis of an extract of the collected medium (10-28). Organic extracts of chemical warfare agents may be analysed directly by GC-MS, but the hydrolysis products of chemical warfare agents usually require derivatization prior to GC-MS analysis (9, 15-18, 20, 22).

More recently researchers have demonstrated the value of LC-MS as a complementary or replacement method for GC-MS, particularly for the confirmation of hydrolysis products of chemical warfare agents in aqueous extracts or samples (37-48), as the hydrolysis products may be analysed directly by LC-MS without the need for additional sample handling and derivatization. In addition, LC-MS has the added benefit that it may also be utilized for the determination of organophosphorus chemical warfare agents and related compounds in aqueous extracts of soil, water, snow and other samples (43-46, 49-51).

Recently a novel mass spectrometric method for sample ionization and analysis, developed by Cooks' group and referred to as desorption electrospray ionization (DESI), was described (52). During the DESI experiment charged droplets in the solvent being electrosprayed impact the surface of interest, desorbing and ionizing the analyte. Ionized large biomolecules and small organic molecules may then be detected by mass spectrometry, often in the tandem mode. Cooks recently reviewed ambient mass spectrometry with an emphasis on the DESI method (53) and included discussion on direct analysis in real time (DART) (54), a related direct analysis approaches.

DESI-MS has been used for a variety of direct analyses (55) including the analysis of pharmaceutical products (56-62), dyes on thin layer chromatography plates (63), explosives on a variety of surfaces (64), polymers (65), alkaloids on plant tissue (66) and chemical warfare agents on solid phase microextraction (SPME) fibers (51, 67). Both the DESI and DART techniques allow rapid, direct sample analysis and have attracted interest in the chemical defence and public security communities due to the minimal sample handling requirements and potential for rapid sample throughput (51, 54, 67). SPME has been applied to many sampling and analysis situations (68), and this method of sampling has been integrated into the chemical warfare agent sampling and analysis strategy developed for counterterrorism purposes in Canada. Direct analysis of SPME fibers by DESI-MS complements existing thermal desorption GC-MS based identification methods and may ultimately enable higher sample throughput with less sample handling.

LC-ESI-MS and DESI-MS have been used at DRDC Suffield for the identification of chemical warfare agents in spiked environmental and office media samples (51, 67) and both approaches will be evaluated for the determination of chemical warfare agents in consumer products. Three consumer products, bottled water, canola oil and corn meal, were selected as candidates for the evaluation and comparative purposes. Each of these media were contaminated with low μg/g levels of chemical warfare agents, levels typically used for evaluation purposes by the Organisation for the Prohibition of Chemical Weapons (OPCW). LC-ESI-MS and LC-ESI-MS/MS methods, developed for the detection of these compounds in aqueous samples and extracts at DRDC Suffield (43-47, 50, 51), were evaluated for the determination of chemical warfare agents in spiked bottled water samples. The headspace above spiked corn meal and canola oil samples were sampled with SPME fibers. Direct analysis of SPME fibers exposed to the headspace above spiked corn meal and canola oil samples by DESI-MS or DESI-MS/MS complements existing mass spectrometric identification methods and may ultimately enable higher sample throughput with less sample handling. MS data used for the identification of all the spiked compounds were acquired in the continuum mode with a resolution of 8000, which typically resulted in mass measurement errors of 0.002 Da or less.

Experimental

Consumer product samples

Samples of three different consumer products were selected for evaluation.

1. Bottled water (Nestle Pure Life)

2. Canola oil (Loblaws No Name).

3. Yellow corn meal (NuPak)

Chemicals

Chemical warfare agent standards and their degradation products were provided by the DRDC Suffield Organic Laboratory. Standard solutions of individual and mixtures of chemical warfare agents were typically prepared at concentrations between 0.4 and 2 mg/mL in dichloromethane. Munitions grade samples of tabun (GA) and mustard (HQ, containing mustard (H), sesquimustard (Q) and related compounds) were prepared similarly.

Hexane, toluene, 1,4-thioxane and dichloromethane were purchased from Aldrich Chemical Company Inc. or Sigma Aldrich.

Bottled water samples

Spiked bottled water samples were prepared in 5.0 mL tapered mini-vials (Mandel Scientific Company) for direct SPME sampling of the water and in 1.8 mL autosampler vials (Agilent) for LC introduction. In all cases 12.5 μL of a 0.4 mg/mL standard mixture containing sarin (GB), triethyl phosphate (TEP), cyclohexyl methylphosphonofluoridate (GF) and soman (GD) were first deposited into the vial. The dichloromethane solvent was allowed to evaporate and 0.5 mL of bottled water was added. Direct SPME sampling of the bottled water spiked at the 10 μg/mL level was conducted at ambient temperature for 2 min with SPME fiber analysis being performed by DESI-MS and DESI-MS/MS. An aliquot (1 μL) of the 10 μg/mL spiked bottle water in the autosampler vial was analysed by LC-ESI-MS and LC-ESI-MS/MS. Bottled water blanks were handled in the same manner.

Polydimethylsiloxane/divinyl benzene (PDMS/DVB) SPME fibers (65 μm film thickness, Supelco) were used throughout the study for water sampling and headspace sampling.

Canola oil samples

Small volumes (typically 5 to 20 μL) of chemical warfare agent standard solutions were added to silanized 20 mL headspace vials (National Scientific Company). The dichloromethane solvent was allowed to evaporate and 1 mL of canola oil was added to the vial. The contents were mixed and allowed to stand for 10 min. Vials containing the spiked canola oil (typically

10 μg/g) were placed in a heated block at temperatures ranging from 40°C to 80 °C (headspace temperature) for 10 min. Headspace sampling was typically conducted for 10 min using SPME fibers. Exposed fibers were analysed by DESI-MS and DESI-MS/MS. Blanks were handled in a similar manner.

Corn meal samples

Small volumes (typically 5 to 20 μL) of chemical warfare agent standard were added to 1 g of corn meal contained in a silanized 20 mL headspace vials (National Scientific Company). The contents were mixed and allowed to stand for 10 min. Vials containing the spiked corn meal (typically 10 μg/g) were placed in a heated block at temperatures ranging from 40°C to 80 °C (headspace temperature) for 10 min. Headspace sampling was typically conducted for 10 min using SPME fibers. Exposed fibers were analysed by DESI-MS and DESI-MS/MS. Blanks were handled in a similar manner.

Vial samples

Small volumes (typically 5 to 20 μL) of chemical warfare agent standard were added to silanized 20 mL headspace vials (National Scientific Company). The dichloromethane solvent was allowed to evaporate and the vials were placed in a heated block at temperatures ranging from ambient to 80 °C (headspace temperature) for 10 min. Headspace sampling was typically conducted for 15 s to 20 min using SPME fibers. Exposed fibers were analysed by DESI-MS and DESI-MS/MS. Blanks were handled in a similar manner.

Toluene and hexane (1 μL, neat) were added to silanized 20 mL headspace vials (National Scientific Company). The vials were kept at ambient temperature (20 to 25 °C) and headspace sampling was typically conducted for 10 s using SPME fibers. Exposed fibers were analysed by DESI-MS and DESI-MS/MS.

LC-ESI-MS analysis

LC-ESI-MS and LC-ESI-MS/MS data were acquired using a Waters QTOF Ultima tandem mass spectrometer equipped with a Z-spray electrospray interface. The electrospray capillary was operated at 3 kV with a sampling cone voltage of 35 V. The collision energy was maintained at 5 V for LC-ESI-MS operation and was varied from 3 to 10 V (depending on the precusor ion selected) for LC-ESI-MS/MS operation. Argon was continually flowing into the collision cell at 9 psi during both LC-ESI-MS and LC-ESI-MS/MS operation. Nitrogen desolvation gas was introduced into the interface (80°C) at a flow rate of 300 L/h and nitrogen cone gas (100 °C) was introduced at a flow rate of 50 L/h. ESI-MS data were acquired from m/z 70 to 500 (0.4 s with a 0.1 s interscan delay) and ESI-MS/MS (product ion mass spectra) data were acquired for the protonated molecular ions of the spiked compounds (0.9 s with a 0.1 s interscan delay). All data were acquired in the continuum mode with a resolution of 8000 (V-mode, 50% valley definition). Mass measurement errors were typically less than 0.002 Da when a lock mass was used.

Chromatographic separations were performed with an Aglient 1100 using a 5% to 50%B gradient over 15 minutes and a flow rate of 10 μl/min: Solvent A (0.1% trifluoroacetic acid in water) and Solvent B (acetonitrile). Separations were performed with an Agilent 50 mm x 0.3 mm i.d. glass lined tube LC column packed with Zorbax SB-C18 (1.8 μm particle size). The Agilent 1100 autosampler was used to introduce 1 μl samples of the spiked bottled water and blanks.

DESI-MS analysis

Similar mass spectrometric operating conditions were employed during DESI-MS and DESI-MS/MS analyses. DESI-MS analyses were initially acquired for TEP with the Z-spray interface glass sleeve removed to allow introduction of the SPME fiber into the region between the electrospray needle and the sampling cone. A laboratory stand was used to hold and position the SPME manual holder so that the fiber could be introduced into an ethanol/water (1:1) mobile phase spraying at 10 μL/min. DESI-MS experiments that vented into the laboratory (without the glass interface sleeve) were not attempted with either chemical warfare agents or the LC mobile phase for safety reasons. A replacement plexiglass sleeve was then machined and a septum port was mounted on the inside of the sleeve to facilitate the safe introduction of exposed SPME fibers. The LC mobile phase, 50:50 acetonitrile/water (0.1% trifluoroacetic acid), was passed through the LC column and sprayed at 10 μL/min during DESI analyses. Nitrogen desolvation gas was introduced into the interface (80°C) at a flow rate of 100 or 300 L/h and nitrogen cone gas (100 °C) was introduced at a flow rate of 50 L/h. MS data were acquired from m/z 70 to 700 (typically 0.3 s with a 0.1 s interscan delay) and MS/MS (product ion mass spectra) data were acquired for the protonated molecular (and other) ions of the spiked compound(s) (typically 0.5 to 0.9 s with a 0.1 s interscan delay). All data were acquired in the continuum mode with a resolution of 8000 (V-mode, 50% valley definition).

Results and discussion

High-field asymmetric waveform ion mobility mass spectrometry (FAIMS-MS) was evaluated for the rapid separation and identification of chemical and biological warfare agents in food and consumer matrices (CRTI-04-0022RD). As part of the evaluation process, DRDC Suffield, the National Laboratory for Chemical Warfare Agent Identification, was to analyse the same consumer matrices using "in-house" mass spectrometric methods. DRDC Suffield has successfully used LC-ESI-MS and LC-ESI-MS/MS to determine the presence of chemical warfare agents in spiked environmental (43-47) and office media (51) samples and recently demonstrated the application of DESI-MS and DESI-MS/MS for the determination of chemical warfare agents in the headspace above spiked office media that might be collected as part of a forensic investigation (51, 67). Consumer products, including bottled water, canola oil and corn meal were spiked at the μg/g levels with chemical warfare agents, levels typically used for evaluation purposes by the Organisation for the Prohibition of Chemical Weapons (OPCW). The bottled water samples were similar to aqueous samples analysed in the past by LC-ESI-MS/MS and these samples were analysed directly using these technique. However, both the canola oil and corn meal samples represented new matrices for which methods have not been previously established. Extraction of chemical warfare agents from, in particular, the canola oil was problematic. As a result, a new technique, DESI-MS/MS, was evaluated for the first time for the determination of chemical warfare agents and related compound in the headspace above spiked canola oil and corn meal samples.

Bottled water samples

Bottled water samples were spiked with chemical warfare agents, knowing that hydrolysis of the spiked chemical warfare agent will occur in hours to days depending on the spiked agent (4). To minimize the possibility of hydrolysis, all analyses were conducted within 30 min of spiking. Figure 1a) illustrates the LC-ESI-MS total-ion-current chromatogram obtained for the bottled water blank. No signal was detected above background during LC-ESI-MS analysis.

Figure 1b) illustrates the LC-ESI-MS total-ion-current chromatogram for the bottled water spiked at the 10 μg/mL level with a standard containing three organophosphorus chemical warfare agents, sarin (GB), cyclohexyl methylphosphonofluoridate (GF) and soman (GD) and the simulant, triethyl phosphate (TEP), a compound that resists hydrolysis. The four compounds (10 ng each) were completely resolved with the GD component beginning to show separation consistent with the presence of two diastereomeric pairs or enantiomers. The acquired mass spectometric data were consistent with standard data acquired for all four components. During these analyses product ion mass spectra were also acquired for the $[M+H]^+$ ions of the spiked compounds. Figure 2 illustrates typical product ion mass spectra for all four compounds spiked into the bottled water sample. A collision energy (CE) that represented a good compromise between $[M+H]^+$ and product ion intensity was selected for each of the spiked compounds. This method of analysis provides excellent specificity (all compounds resolved by LC prior to MS characterization), good full scanning detection limits (typically 50 to 500 pg per compound) but requires a relatively long analysis time (30 min).

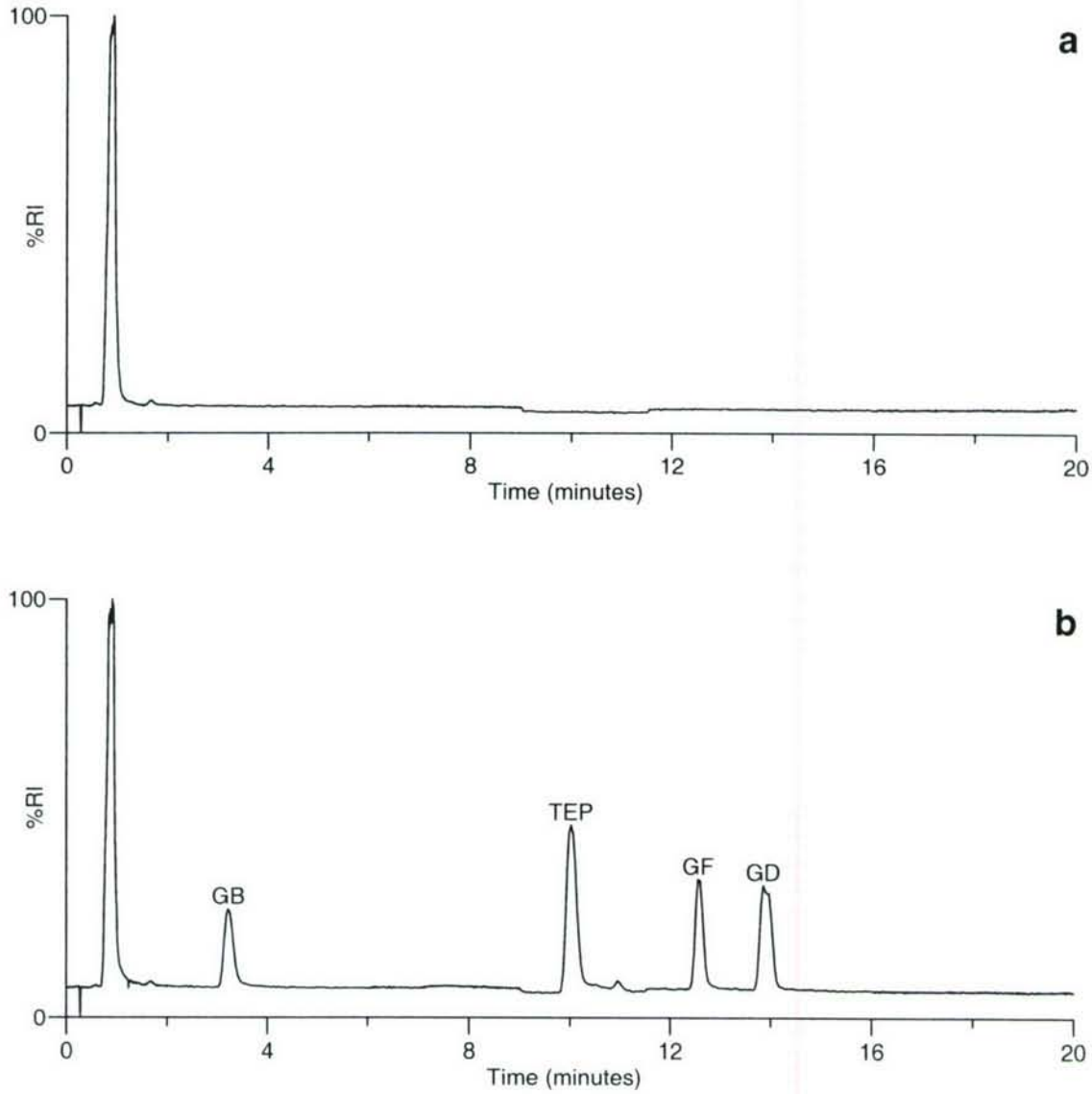

Figure 1. *LC-ESI-MS total-ion-current (m/z 70 to 500) chromatogram for a) bottled water blank and b) bottle water spiked at the 10 µg/mL level with sarin (GB), triethyl phosphate (TEP), cyclohexyl methylphosphonofluoridate (GF) and soman (GD). Product ion mass spectra for the $[M+H]^+$ ion for each of the spiked compounds were also acquired during this analysis. Product mass spectra for m/z 141, m/z 183, m/z 181 and m/z 183 were acquired from 2 to 6 min, 9 to 11.5 min, 11.5 to 13.3 min and 13.3 to 16 min, respectively (refer to Figure 2).*

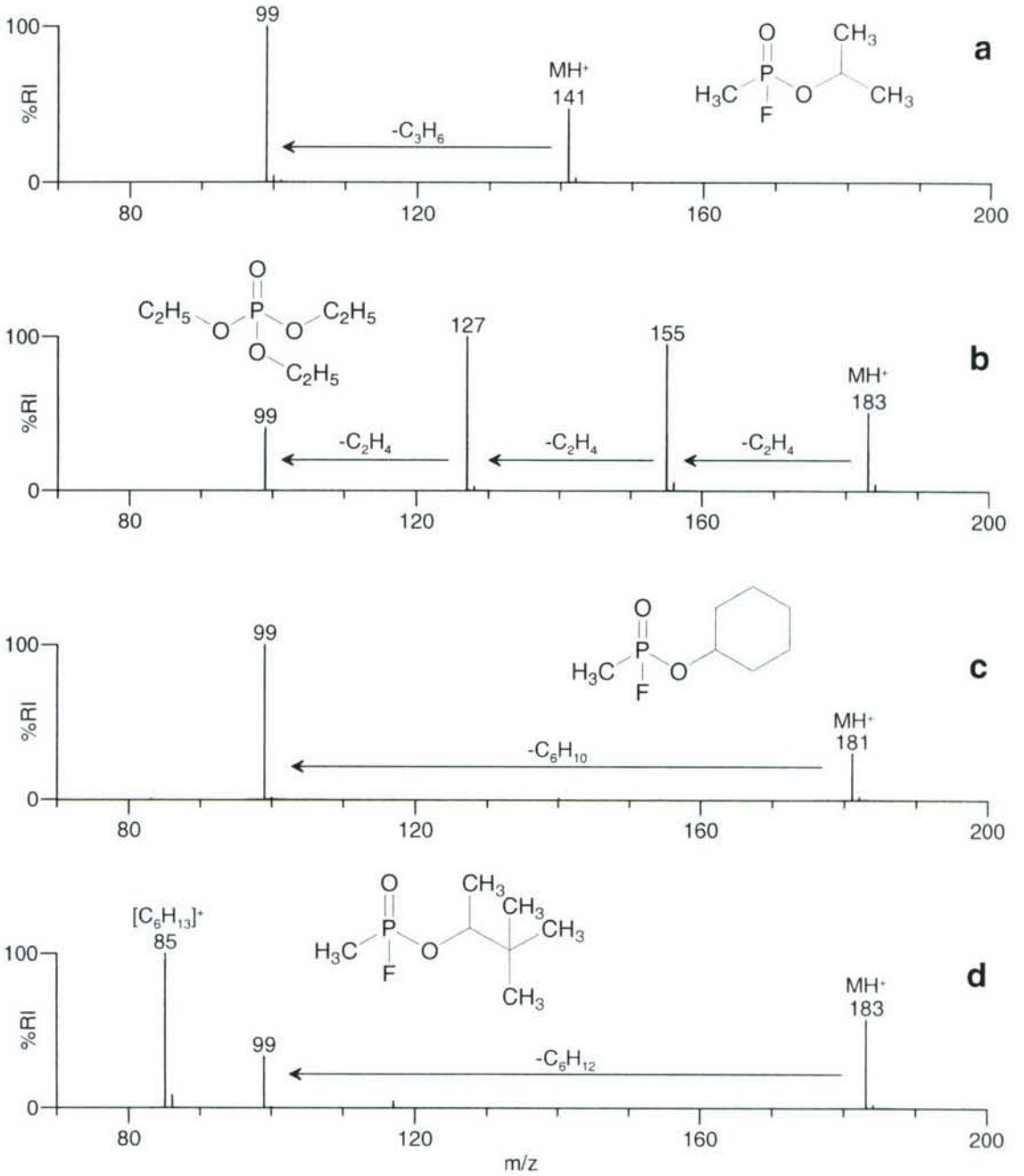

Figure 2. *Product ion mass spectra acquired for a) sarin (CE: 3V), b) triethyl phosphate (CE: 10V), c) cyclohexyl methylphosphonofluoridate (CE: 4V) and d) soman (CE: 3V) during LC-ESI-MS/MS analysis of a bottle water sample spiked at the 10 µg/mL level with the these four compounds .*

The SPME fibers used for headspace sampling can also be used to sample aqueous samples containing chemical warfare agents. Bottled water spiked at the 10 µg/mL level with GB, GF, GD and TEP, was sampled at ambient temperature for 2 min using a polydimethylsiloxane/divinyl benzene (PDMS/DVB) SPME fiber. Figure 3 illustrates the

analysis of the SPME fiber by DESI-MS and DESI-MS/MS. In a matter of seconds following fiber insertion, mass spectrometric data consistent with the presence of all four spiked compounds was acquired. Figure 4 illustrates the analysis of a bottled water blank under identical conditions. No signal was detected above the background during DESI-MS or DESI-MS/MS of the blank sample.

Data were acquired during DESI-MS and DESI-MS/MS for up to 10 min during these experiments but the acquisition time could easily be shortened since most of the analyte was introduced into the mass spectrometer during the first minute after SPME fiber insertion. A total analysis time of less than 3 minutes would be achievable provided the concentration of analyte on the fiber is not excessive. In those cases it may take additional time to vent volatilized analyte from the ESI interface. Direct analyses without chromatographic separation often suffers from a specificity standpoint, even with the use of tandem mass spectrometry. This was evident during DESI-MS/MS of the bottled water spiked with GB, GF, GD and TEP. DESI-MS/MS successfully resolved GB and GF from GD and TEP, but the method could not resolve these two components that exhibited $[M+H]^+$ ions of the same nominal mass. The overall sensitivity of the DESI-MS/MS method was similar to LC-ESI-MS/MS method, taking into account the higher sample loads typically associated with SPME headspace sampling (67).

Canola oil and corn meal samples

The headspace above spiked and blank canola oil samples were analysed by DESI-MS to avoid extraction difficulties issues associated with this media. The blank canola oil sample was heated and the headspace (80°C) above it was sampled with a polydimethylsiloxane/divinyl benzene (PDMS/DVB) SPME fiber. The fiber was analysed by DESI-MS (Figure 5), where the ions selected in the reconstructed-ion-current chromatograms corresponded to the $[M+H]^+$ ions that would be used during DESI-MS/MS analysis of sarin (GB) (m/z 141), mustard (H) (m/z 159), tabun (GA) (m/z 163), cyclohexyl methylphosphonofluoridate (GF) (m/z 181), soman (GD) (m/z 183) and O-ethyl S-[2-(diisopropylamino)ethyl] methylphosphonothiolate (VX) (m/z 267). There was significant signal associated with introduction of the fiber, with the mass spectrum in Figure 6 being typical of a blank fiber exposed to the headspace above heated canola oil. No background interference was noted for any of the target chemical warfare agents with the exception of GB. An interference ion with the same nominal mass, m/z 141, was detected as a minor ion in the canola oil blank (Figure 6), but the GB ion at m/z 141.048 could be completely resolved from this ion at the resolution employed during analysis (8000, 50% valley definition). It should be noted that at lower headspace temperatures typically used for GB sampling (e.g., 40°C) this background ion (and most others) were not observed.

Similar data were acquired for SPME samples of the headspace above blank corn meal samples. Figure 7 illustrates the DESI-MS total-ion-current and reconstructed-ion-current chromatograms obtained following analysis of a PDMS/DVB SPME fiber exposed to the headspace (80°C) above heated corn meal. Background ions were minimal (Figure 8) and no background ions were observed that would interfere with headspace sampling and analysis of corn meal exposed to the common chemical warfare agents.

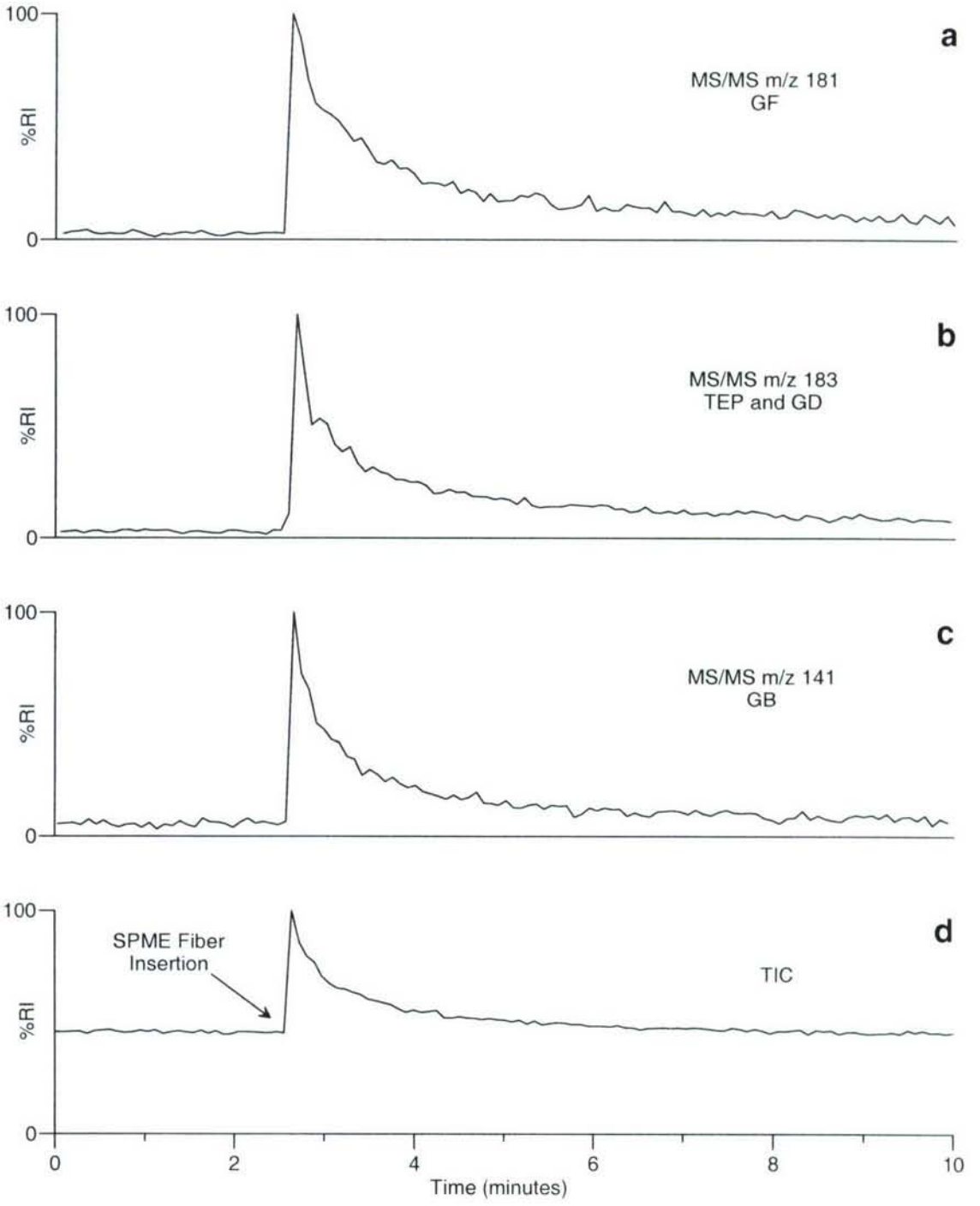

Figure 3. *DESI-MS and MS/MS analysis of a SPME fiber used to sample bottled water spiked at the 10 µg/mL level with cyclohexyl methylphosphonofluoridate (GF), triethyl phosphate (TEP), soman (GD) and sarin (GB). The SPME fiber was inserted into the water for 2 min at ambient temperature. Product ion chromatograms acquired for a) m/z 181, b) m/z 183 and c) m/z 141. d) Total-ion-current (m/z 70 to 700) chromatogram obtained during the same analysis. All four spiked compounds were detected.*

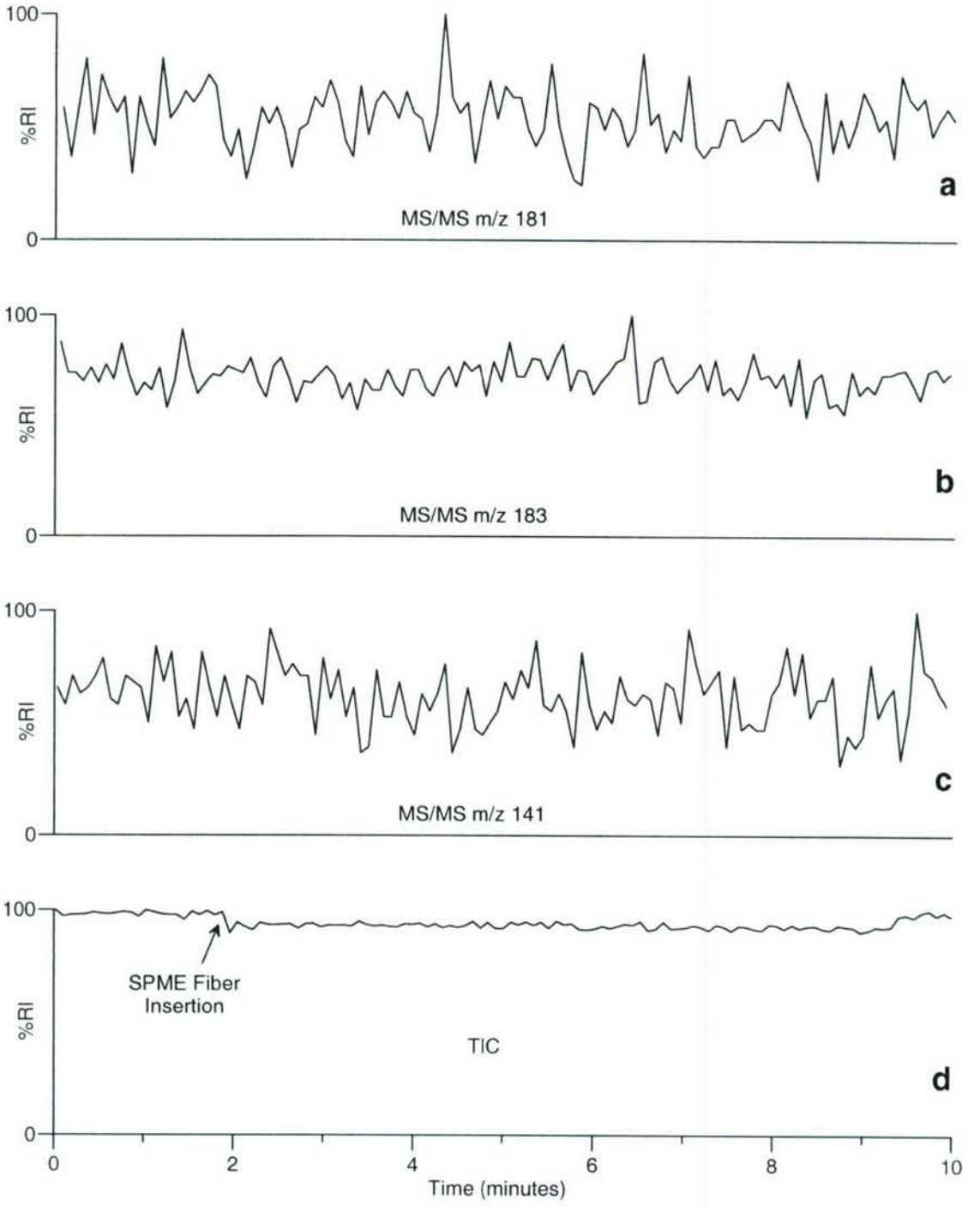

Figure 4. *DESI-MS and MS/MS analysis of a SPME fiber used to sample bottled water blank. The SPME fiber was inserted into the water for 2 min at ambient temperature. Product ion chromatograms acquired for a) m/z 181, b) m/z 183 and c) m/z 141. d) Total-ion-current (m/z 70 to 700) chromatogram obtained during the same analysis.*

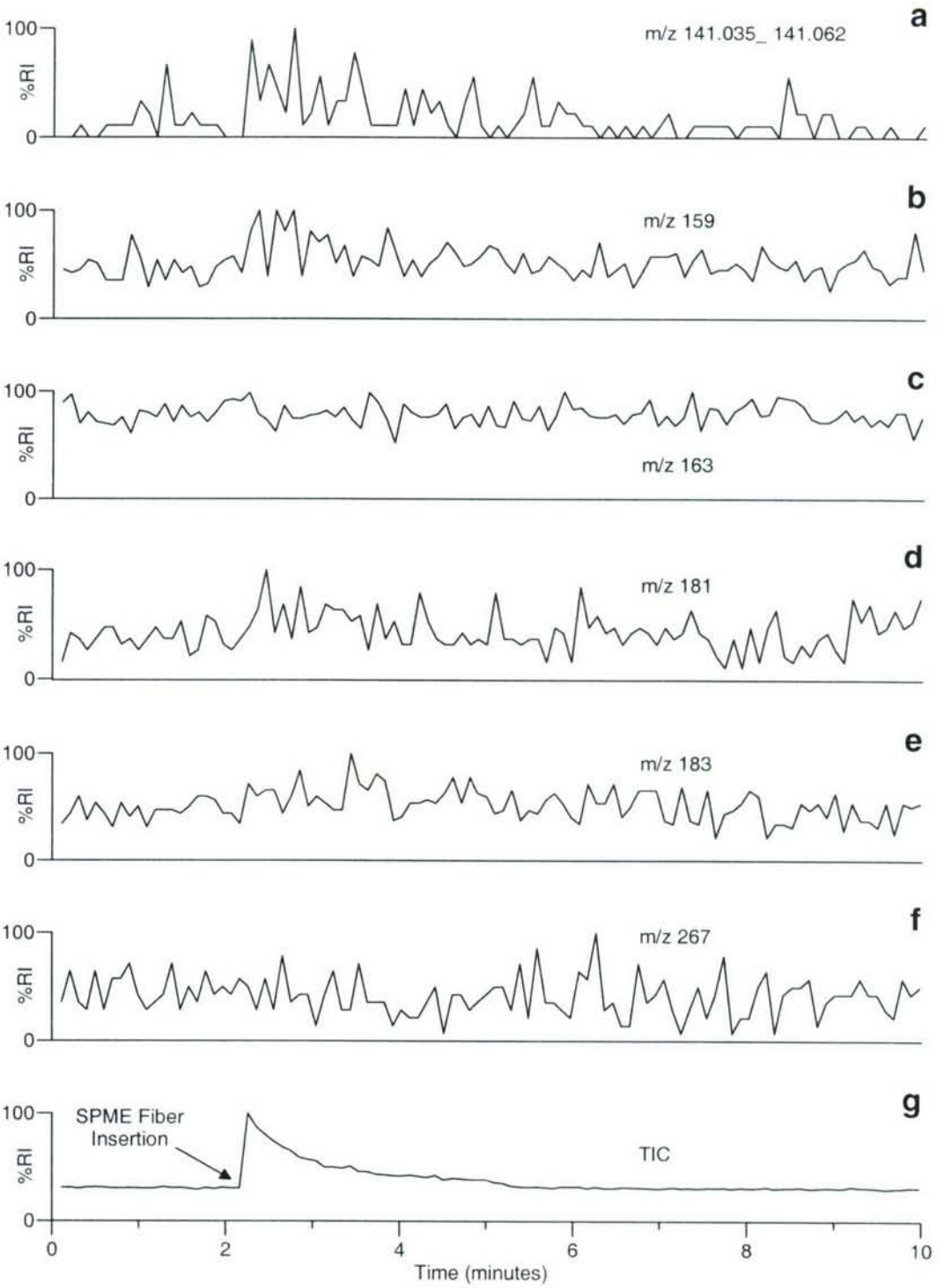

Figure 5. *DESI-MS analysis of a SPME fiber used to sample the headspace (20 min at 80 °C) above a canola oil blank. Reconstructed-ion-current chromatograms for a) m/z 141 (window narrowed to exclude a background ion of the same nominal mass as sarin), b) m/z 159, c) m/z 163, d) m/z 181, e) m/z 183 and f) m/z 267. g) Total-ion-current (m/z 70 to 700) chromatogram.*

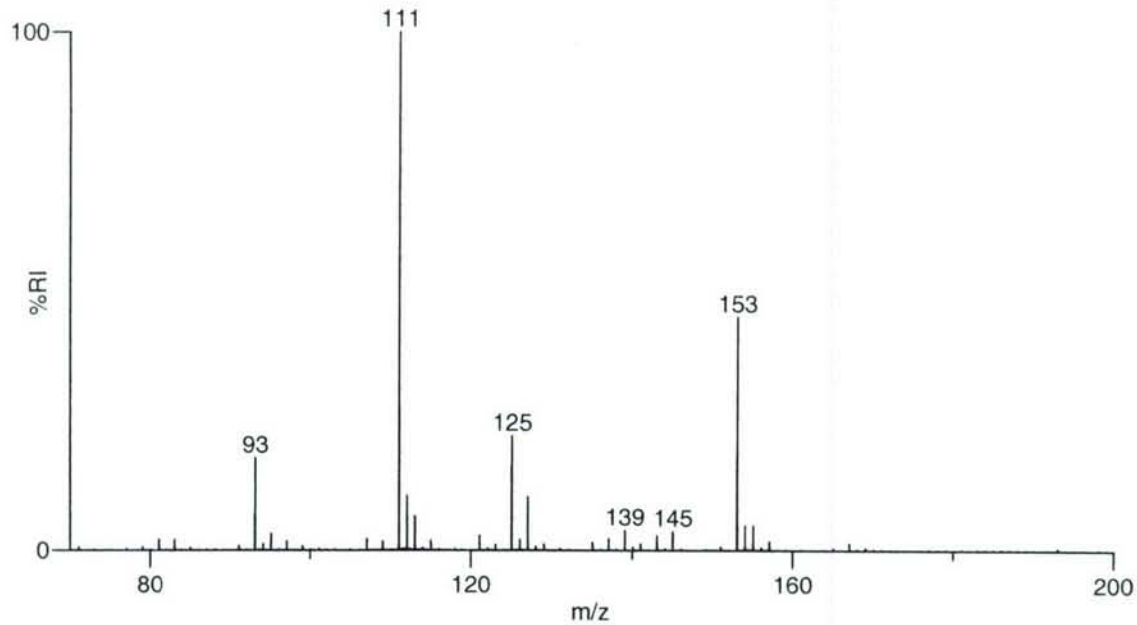

Figure 6. *Typical ESI-MS data acquired during DESI-MS analysis of the SPME fiber used to sample the canola oil blank (refer to Figure 5).*

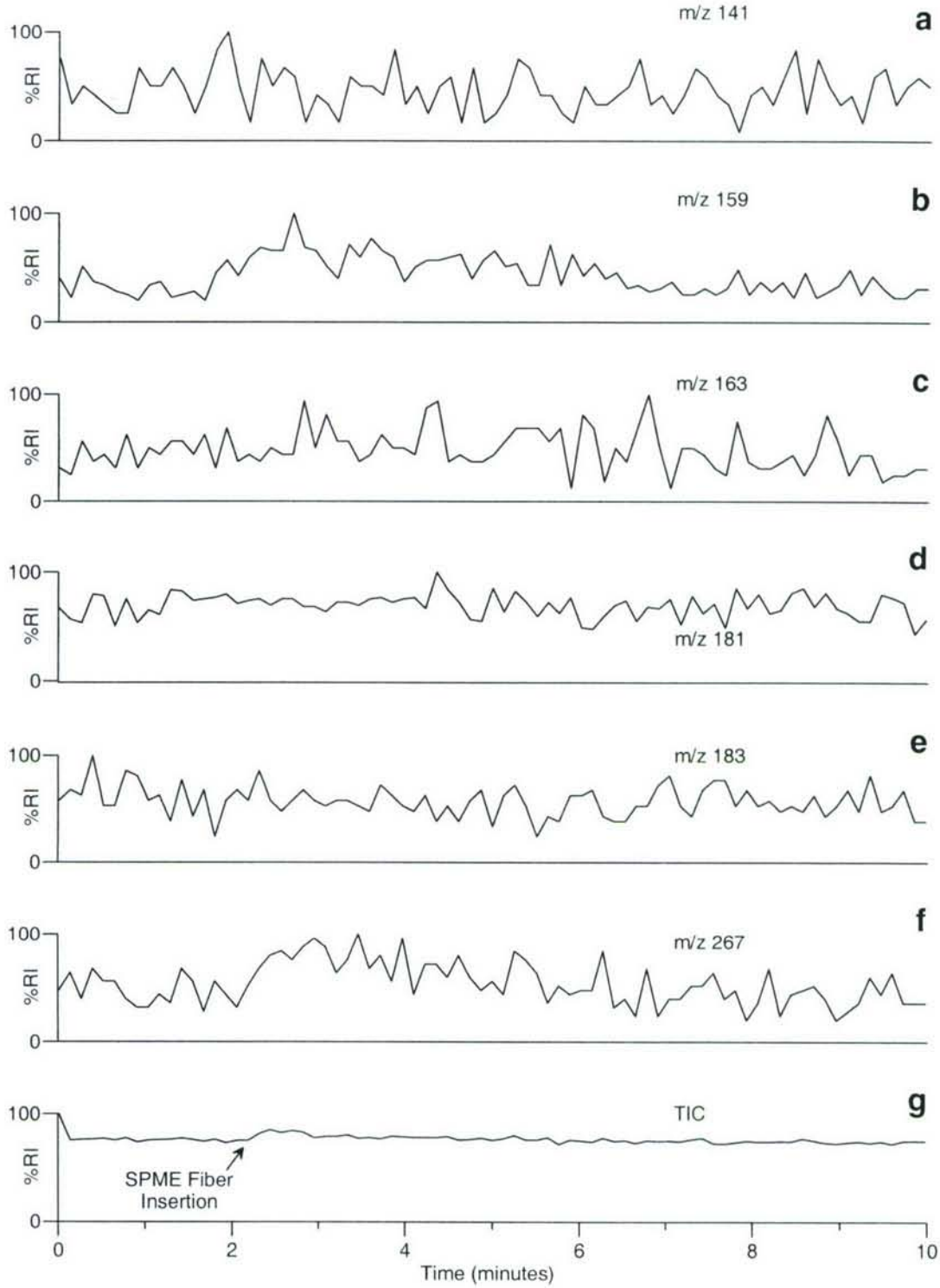

Figure 7. *DESI-MS analysis of a SPME fiber used to sample the headspace (5 min at 80 °C) above a corn meal blank. Reconstructed-ion-current chromatograms for a) m/z 141, b) m/z 159, c) m/z 163, d) m/z 181, e) m/z 183 and f) m/z 267. g) Total-ion-current (m/z 70 to 700) chromatogram.*

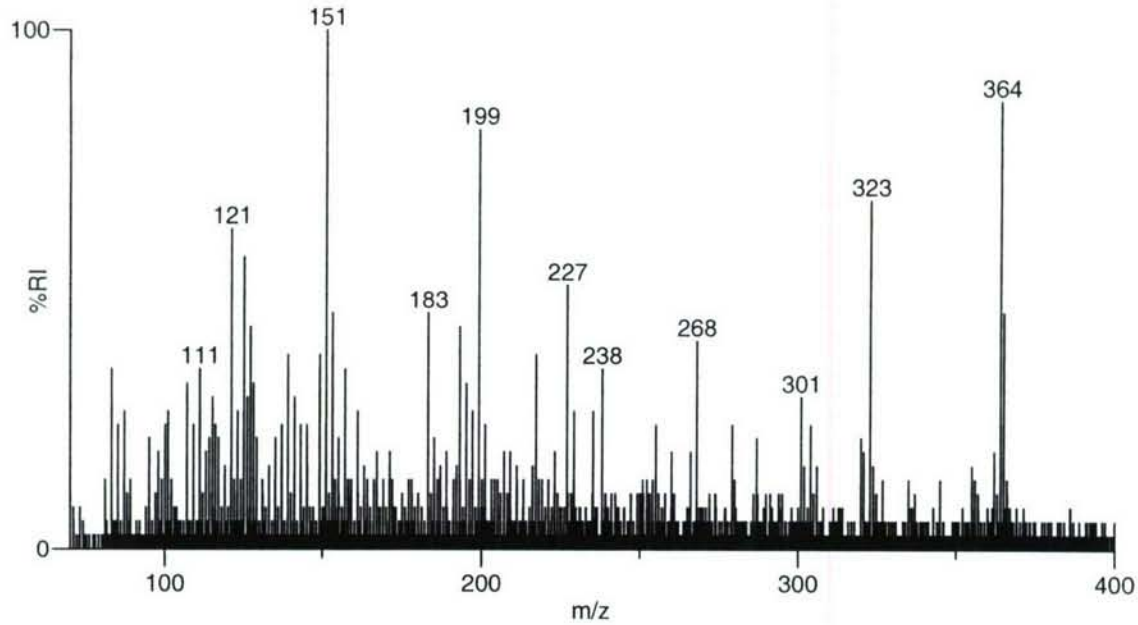

Figure 8. *Typical ESI-MS data acquired during DESI-MS analysis of the SPME fiber used to sample the corn meal blank (refer to Figure 7).*

DESI-MS and DESI-MS/MS data were acquired for SPME fibers exposed to the headspace above µg quantities of each of TEP, GB, GA, GD, GF, VX and H and for SPME fibers exposed to the headspace above canola oil and corn meal samples spiked at the µg/g level with the same analytes. All SPME sampling was performed using 20 mL headspace sampling vials with higher headspace temperatures and longer sampling times being employed for the less volatile analytes.

Figures 9 through 15 illustrate typical data obtained following DESI-MS/MS analysis of SPME fibers used to sample the headspace above TEP, GB, GA, GD, GF, VX and H, respectively, and the same analytes spiked into canola oil and corn meal at the µg/g level. All the chemical warfare agents and TEP were detected by DESI-MS/MS following sampling of the vial spiked at the µg level, with relatively short sampling times. Typical product ion mass spectra for each of the chemical warfare agents and TEP, with the collision energy (CE) used during DESI-MS/MS analysis have been inserted into each of Figures 9 through 15.

Longer SPME headspace sampling times were required to collect sufficient analyte for DESI-MS/MS of the spiked canola oil and corn meal samples. Canola oil proved to be a fairly difficult matrix and not every spiked compound was sampled onto the SPME fiber. TEP (Figure 9b)), GB (Figure 10b)) and GA (Figure 11b)) were readily detected following DESI-MS/MS analysis. GD (Figure 22b)) and GF (Figure 13b)), two relatively non-polar chemical warfare agents, appear to prefer the canola oil to the headspace. Only a low signal was observed during DESI-MS/MS analysis of the SPME fiber used to sample the headspace above both GD and GF spiked into canola oil.

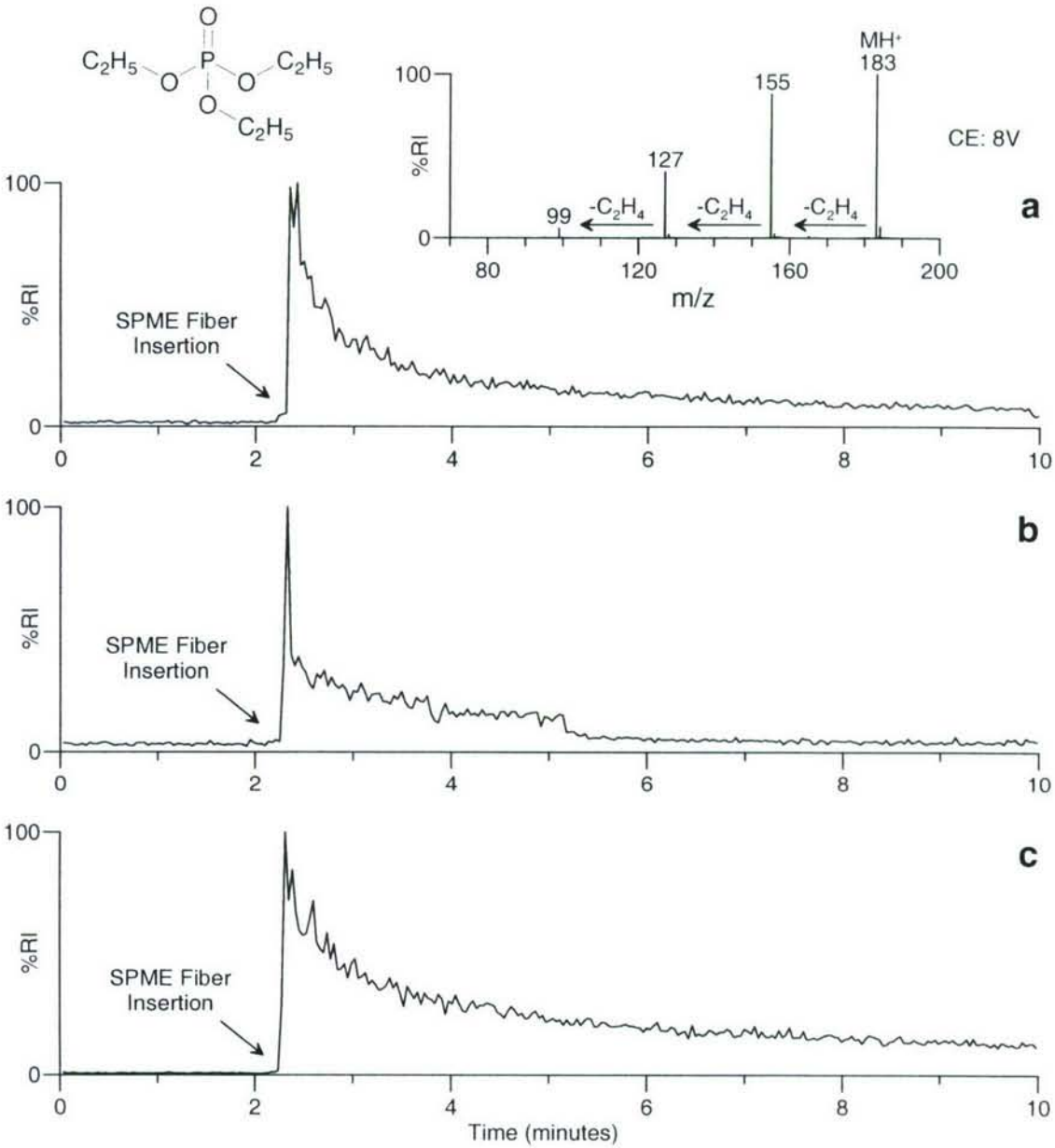

Figure 9. *DESI-MS/MS chromatograms for m/z 183 obtained during analysis of a) a SPME fiber used to sample the headspace (15 s at 40 °C) above 0.5 µg of triethyl phosphate (TEP), b) a SPME fiber used to sample the headspace (10 min at 40 °C) above canola oil spiked at the 5 µg/g level with TEP and c) a SPME fiber used to sample the headspace (10 min at 40 °C) above corn meal spiked at the 5 µg/g level with TEP. Inset: typical product ion mass spectrum for TEP.*

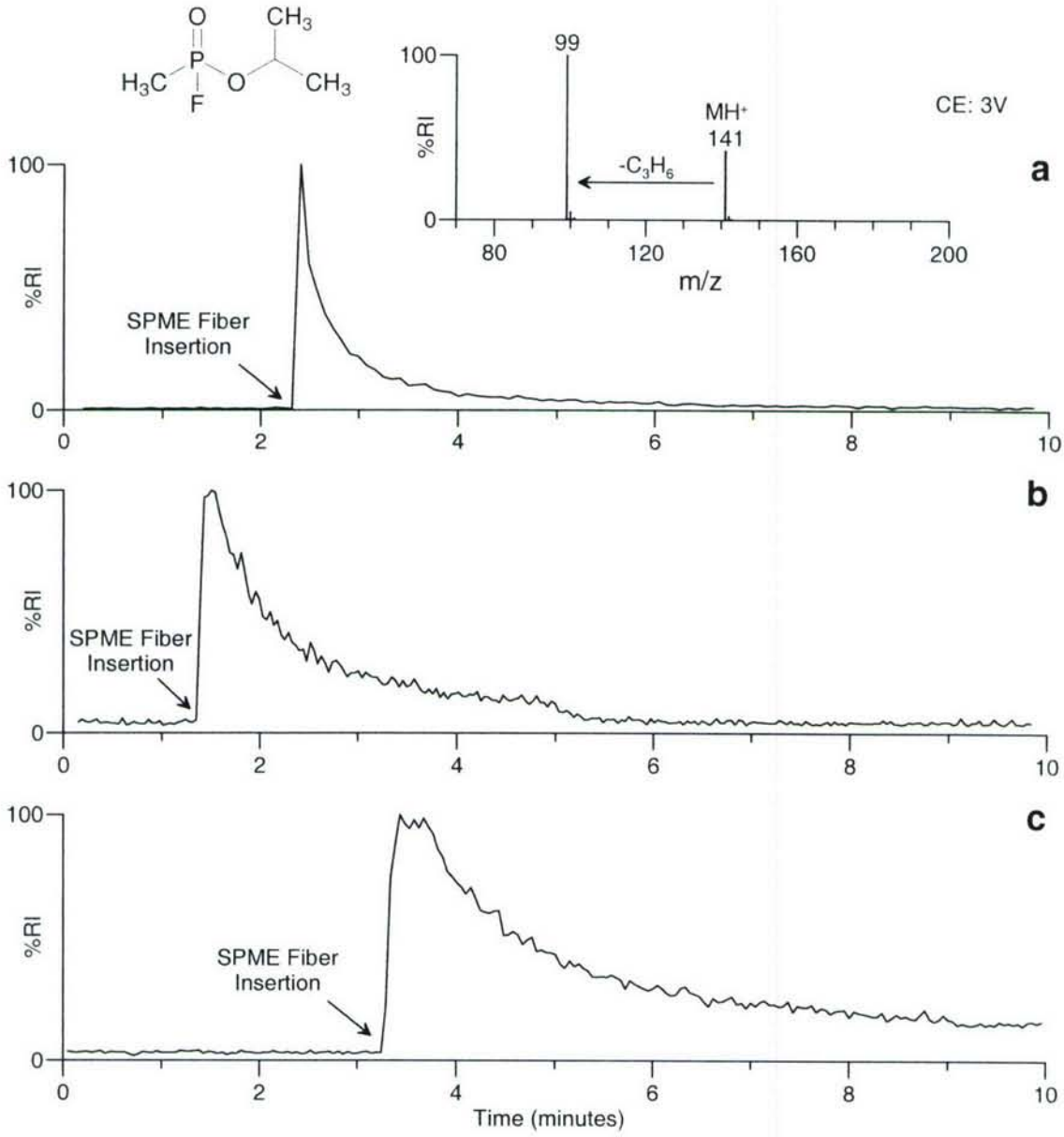

Figure 10. *DESI-MS/MS chromatograms for m/z 141 obtained during analysis of a) a SPME fiber used to sample the headspace (15 s at 40 °C) above 5 µg of sarin (GB), b) a SPME fiber used to sample the headspace (10 min at 40 °C) above canola oil spiked at the 5 µg/g level with GB and c) a SPME fiber used to sample the headspace (10 min at 40 °C) above corn meal spiked at the 5 µg/g level with GB. Inset: typical product ion mass spectrum for GB.*

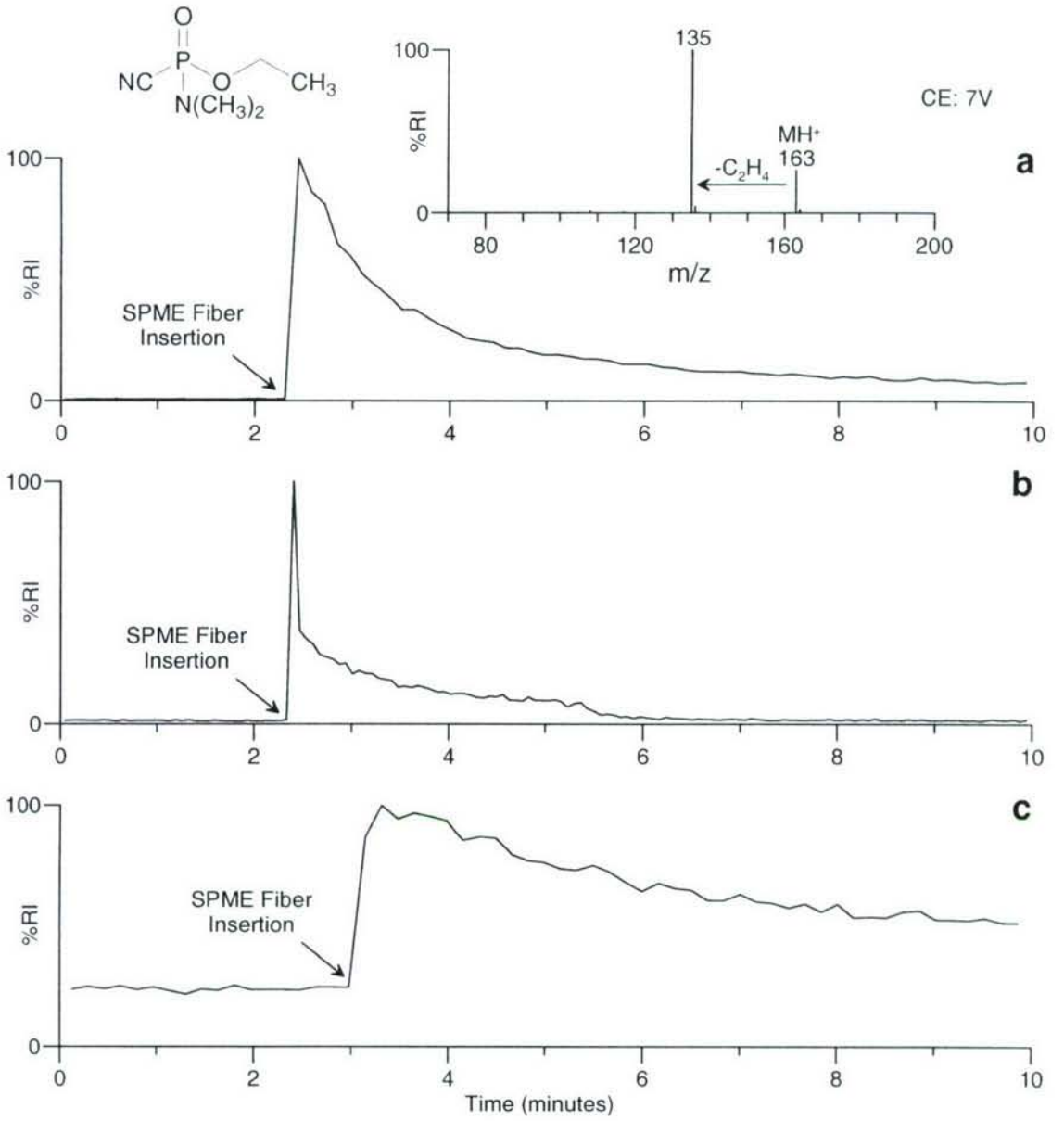

Figure 11. *DESI-MS/MS chromatograms for m/z 163 obtained during analysis of a) a SPME fiber used to sample the headspace (2 min at 40 °C) above 0.5 µg of tabun (GA), b) a SPME fiber used to sample the headspace (10 min at 40 °C) above canola oil spiked at the 15 µg/g level with GA and c) a SPME fiber used to sample the headspace (10 min at 40 °C) above corn meal spiked at the 15 µg/g level with GA. Inset: typical product ion mass spectrum for GA.*

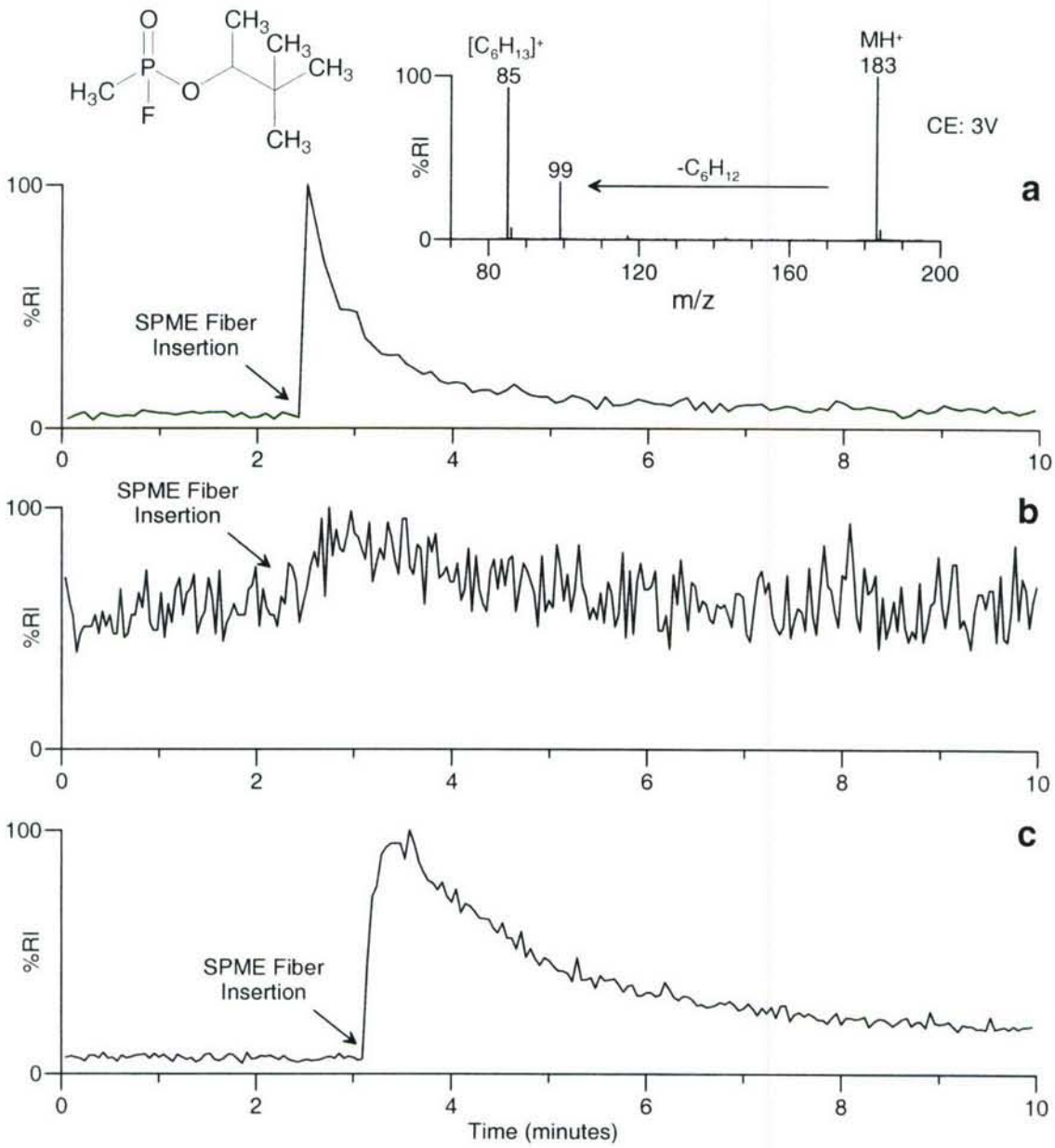

Figure 12. *DESI-MS/MS chromatograms for m/z 183 obtained during analysis of a) a SPME fiber used to sample the headspace (15 s at 40 °C) above 5 µg of soman (GD), b) a SPME fiber used to sample the headspace (10 min at 40 °C) above canola oil spiked at the 10 µg/g level with GD and c) a SPME fiber used to sample the headspace (10 min at 40 °C) above corn meal spiked at the 10 µg/g level with GD. Inset: typical product ion mass spectrum for GD.*

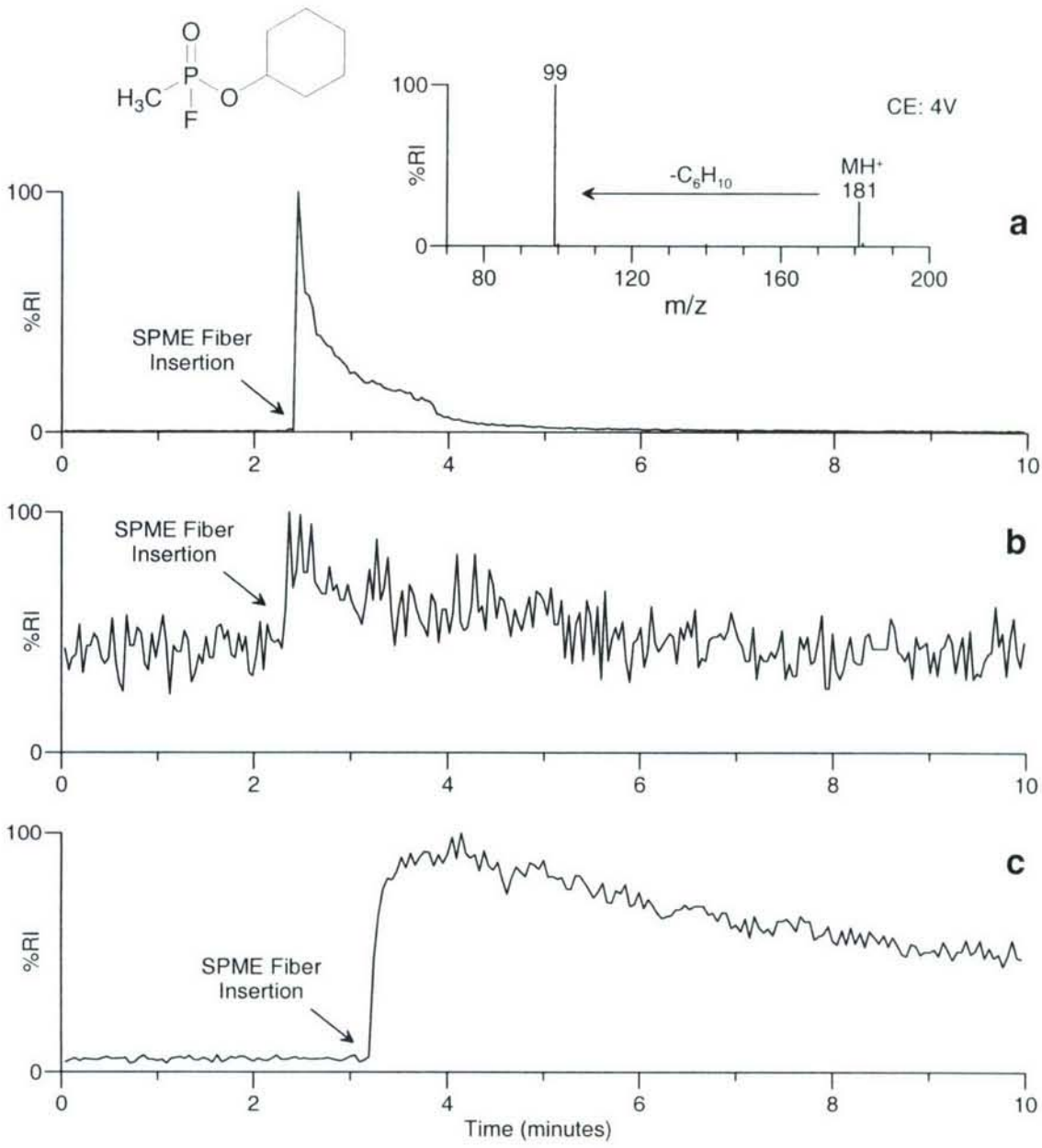

Figure 13. *DESI-MS/MS chromatograms for m/z 181 obtained during analysis of a) a SPME fiber used to sample the headspace (15 sec at 40 °C) above 5 µg of cyclohexyl methylphosphonofluoridate (GF), b) a SPME fiber used to sample the headspace (10 min at 40 °C) above canola oil spiked at the 10 µg/g level with GF and c) a SPME fiber used to sample the headspace (10 min at 40 °C) above corn meal spiked at the 10 µg/g level with GF. Inset: typical product ion mass spectrum for GF.*

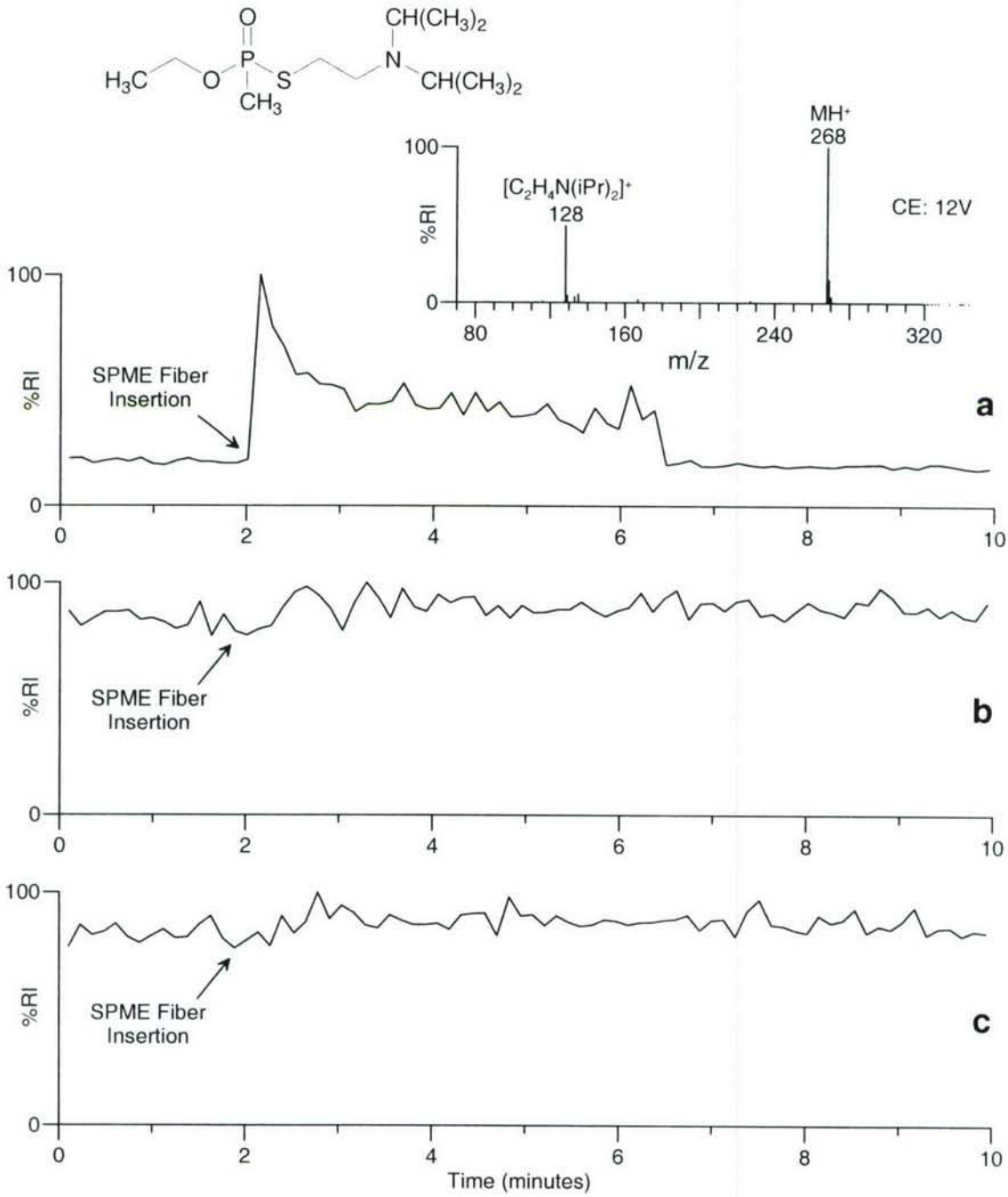

Figure 14. *DESI-MS/MS chromatograms for m/z 267 obtained during analysis of a) a SPME fiber used to sample the headspace (5 min at 80 °C) above 10 µg of VX, b) a SPME fiber used to sample the headspace (20 min at 80 °C) above canola oil spiked at the 10 µg/g level with VX and c) a SPME fiber used to sample the headspace (10 min at 80 °C) above corn meal spiked at the 10 µg/g level with VX. Inset: typical product ion mass spectrum for VX.*

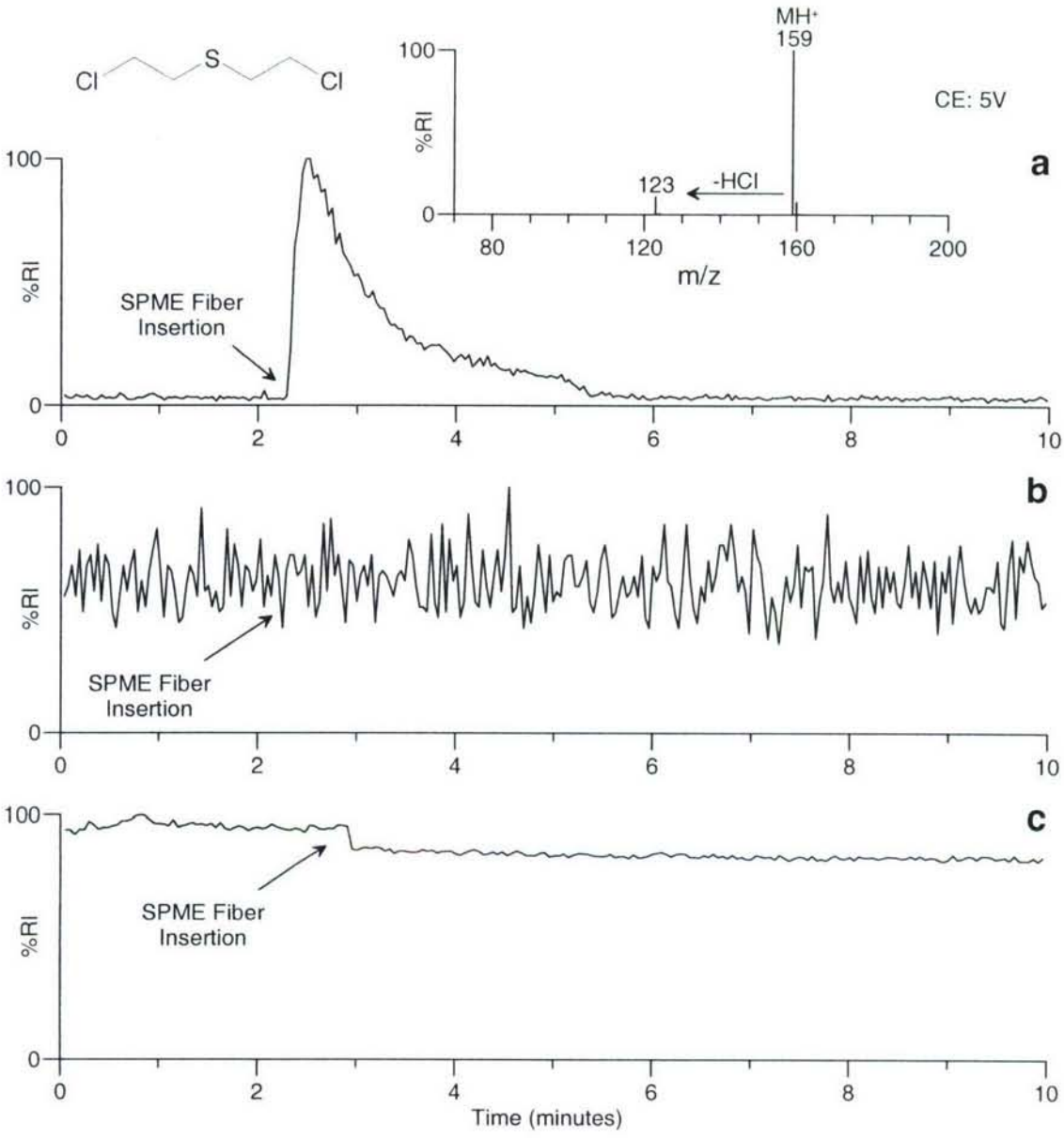

Figure 15. *DESI-MS/MS chromatograms for m/z 159 obtained during analysis of a) a SPME fiber used to sample the headspace (10 min at 40 °C) above 10 µg of mustard (H), b) a SPME fiber used to sample the headspace (10 min at 40 °C) above canola oil spiked at the 10 µg/g level with H and c) a SPME fiber used to sample the headspace (10 min at 40 °C) above corn meal spiked at the 10 µg/g level with H. Inset: typical product ion mass spectrum for H.*

SPME headspace sampling and DESI-MS/MS analysis of the spiked corn meal samples was more successful. TEP (Figure 9c)), GB (Figure 10 c)), GA (Figure 11c)), GD (Figure 12c)) and GF (Figure 13c)) were all readily detected. Several of the chromatograms exhibiting profiles with significant tailing (e.g., Figure 13c)). This did not compromise the identification of the spiked analytes and was likely due to the use of a lower desolvation flow rate (100 L/hr) during some of the earlier experiments with spiked corn meal.

VX, the chemical warfare agent with the lowest volatility, was sampled in the headspace of the vial at an elevated temperature and with lower sensitivity than the other chemical warfare agents and could not be detected in the spiked media samples (Figure 14). The maximum headspace temperature that could be achieved with the heating block was 80°C. More efficient headspace sampling might be possible with a higher headspace temperature, which might also enable the detection of VX in spiked corn meal and canola oil samples.

H cannot be analysed by LC-ESI-MS/MS as it does not ionize under ESI conditions. It does however produce an interpretable mass spectrum during DESI-MS or DESI-MS/MS analysis, which suggests an ionization mechanism that differs from conventional electrospray (discussion to follow in Ionization mechanisms section). H was readily detected following SPME headspace sampling and DESI-MS/MS analysis of H in a vial but this relatively volatile compound seems to prefer the media to the headspace (Figure 15). Similar SPME sampling issues were also observed during analysis of spiked office media (67).

Munition grade agent analyses

Terrorist use of chemical warfare agents may involve the use of crude or munitions grade chemical warfare agent that contains not only the chemical warfare agent but also related co-synthetic, degradation or other products. Identification of these additional sample components could be helpful in establishing a link between the chemical warfare agent used in the incident and a source, or provide an indication of synthetic route used to prepare the chemical warfare agent. A munitions grade sample of GA containing related organophosphorus compounds (69) and a munitions grade sample of mustard, HQ (70), containing H, sesquimustard (Q) and related organosulfur compounds were selected to evaluate the applicability of SPME headspace sampling and DESI-MS/MS analysis for the identification purpose.

The munitions grade GA sample containing approximately 70% GA, was spiked into canola oil at the 20 μg/g level and the headspace was sampled using a polydimethylsiloxane/divinyl benzene (PDMS/DVB) SPME fiber. Figure 16 illustrates the DESI-MS total-ion-current chromatogram obtained during analysis of the fiber. The mass spectrum obtained contained $[M+H]^+$ ions for GA and three related organophosphorus components, ethyl tetramethylphosphorodiamidate, diethyl dimethylphosphoramidate and ethyl isopropyl dimethylphosphoramidate. A product ion was also observed for GA (m/z 135) in the acquired mass spectrum.

HQ samples were deposited into a 20 mL headspace sampling vials and sampled at headspace temperatures up to 80°C in a effort to acquire DESI-MS data for Q. The effort was unsuccessful for Q but $[M+H]^+$ ions for several related organosulfur compounds were acquired during DESI-MS analysis of the PDMS/DVB SPME fiber (Figure 17). Two of the compounds, 1,4-thioxane and 1,4-dithiane, have been reported as common impurities in munitions grade mustard samples (70). Two sample components remain unidentified even after acquisition of MS/MS data. However the elemental composition of the unknowns appears to be C_4H_7SOCl and $C_4H_8SOCl_2$ based on acquired high resolution data for their $[M+H]^+$ ions.

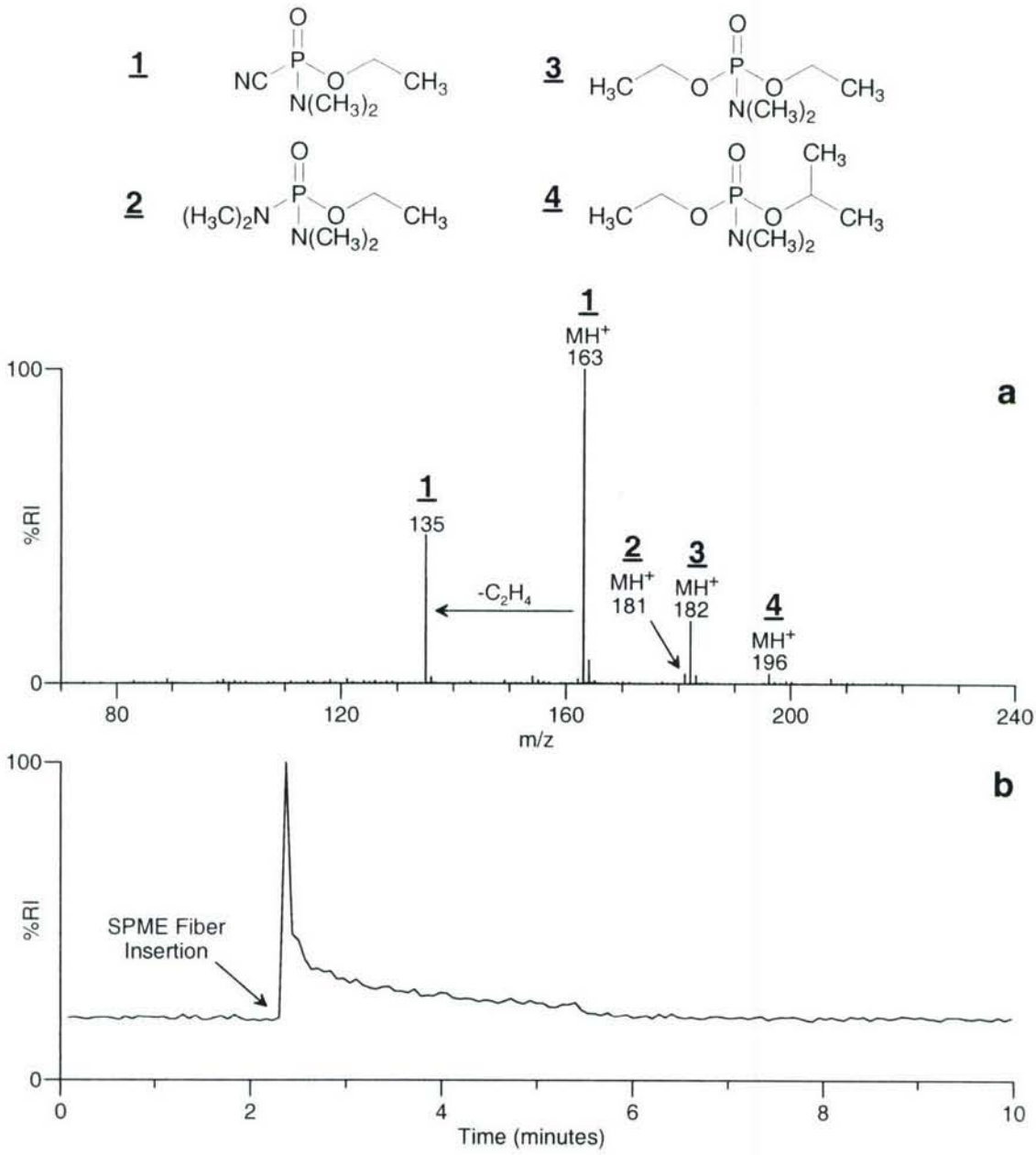

Figure 16. *a) ESI-MS data acquired during DESI-MS analysis of a SPME fiber used to sample the headspace (10 min at 40 °C) above canola oil spiked at the 20 µg/g level with a munitions grade sample of tabun (GA). Tabun and three related compounds were detected. b) DESI-MS total-ion current (m/z 70 to 700) chromatogram obtained during this analysis.*

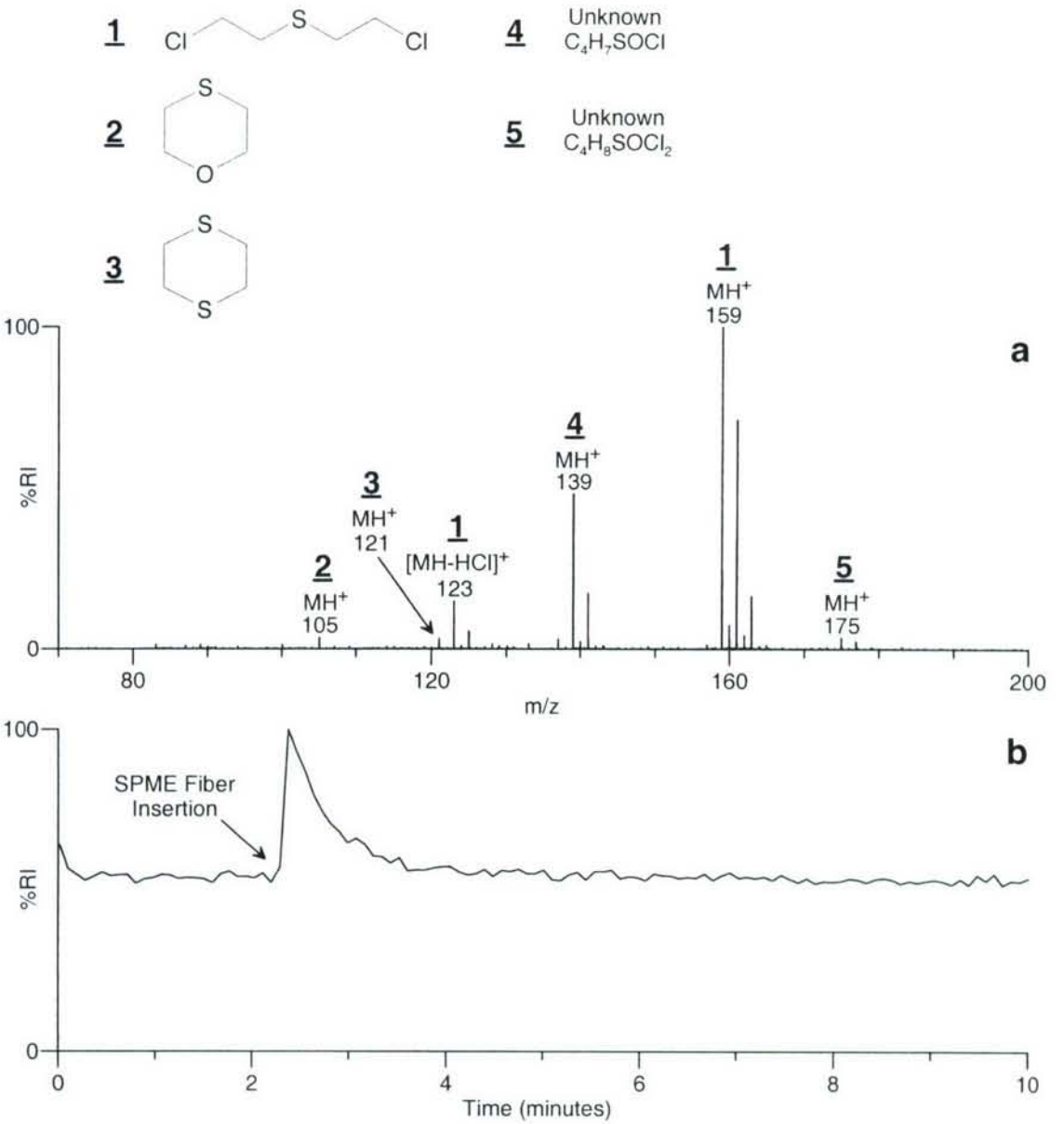

Figure 17. *a) ESI-MS data acquired during DESI-MS analysis of a SPME fiber used to sample the headspace (10 min at 40 °C) above 40 µg of a munitions grade mustard sample, HQ. Mustard (H) and four related compounds were detected. Sesquimustard (Q) was not detected. b) DESI-MS total-ion current (m/z 70 to 700) chromatogram obtained during this analysis.*

Hydrolysis products of chemical warfare agents

The hydrolysis products of chemical warfare agents may be identified in aqueous samples or extracts by LC-ESI-MS or LC-ESI-MS/MS (9), with this technique often being preferred over derivatization and identification by GC-MS (8). Three hydrolysis products, isopropyl methylphosphonic acid (hydrolysis product of GB), pinacolyl methylphosphonic acid (hydrolysis product of GD) and thiodiglycol (hydrolysis product of H) were placed in individual 20 mL headspace sampling vial to evaluate SPME headspace sampling and analysis by DESI-MS and DESI-MS/MS.

Figures 18 and 19 illustrate the DESI-MS total-ion-current chromatogram and acquired product ion mass spectra for isopropyl methylphosphonic acid (and its dimer) and pinacolyl methylphosphonic acid (and its dimer), respectively. Both compounds were identified with a higher headspace temperature (80°C) being used for headspace sampling of the pinacolyl methylphosphonic acid.

Attempts to recover isopropyl methylphosphonic acid or pinacolyl methyl phosphonic acid from canola oil were largely unsuccessful. Only a trace amount of isopropyl methylphosphonic acid was observed following SPME headspace sampling and DESI-MS/MS analysis of a spiked canola oil sample.

Thiodiglycol was identified following SPME headspace sampling and DESI-MS and DESI-MS/MS analysis of fibers exposed to thiodiglycol and canola oil spiked with thiodiglycol (Figure 20). The product ion mass spectrum for thiodiglycol exhibited a significant product ion at m/z 105, consistent with ESI-MS/MS acquired during LC-ESI-MS/MS analysis.

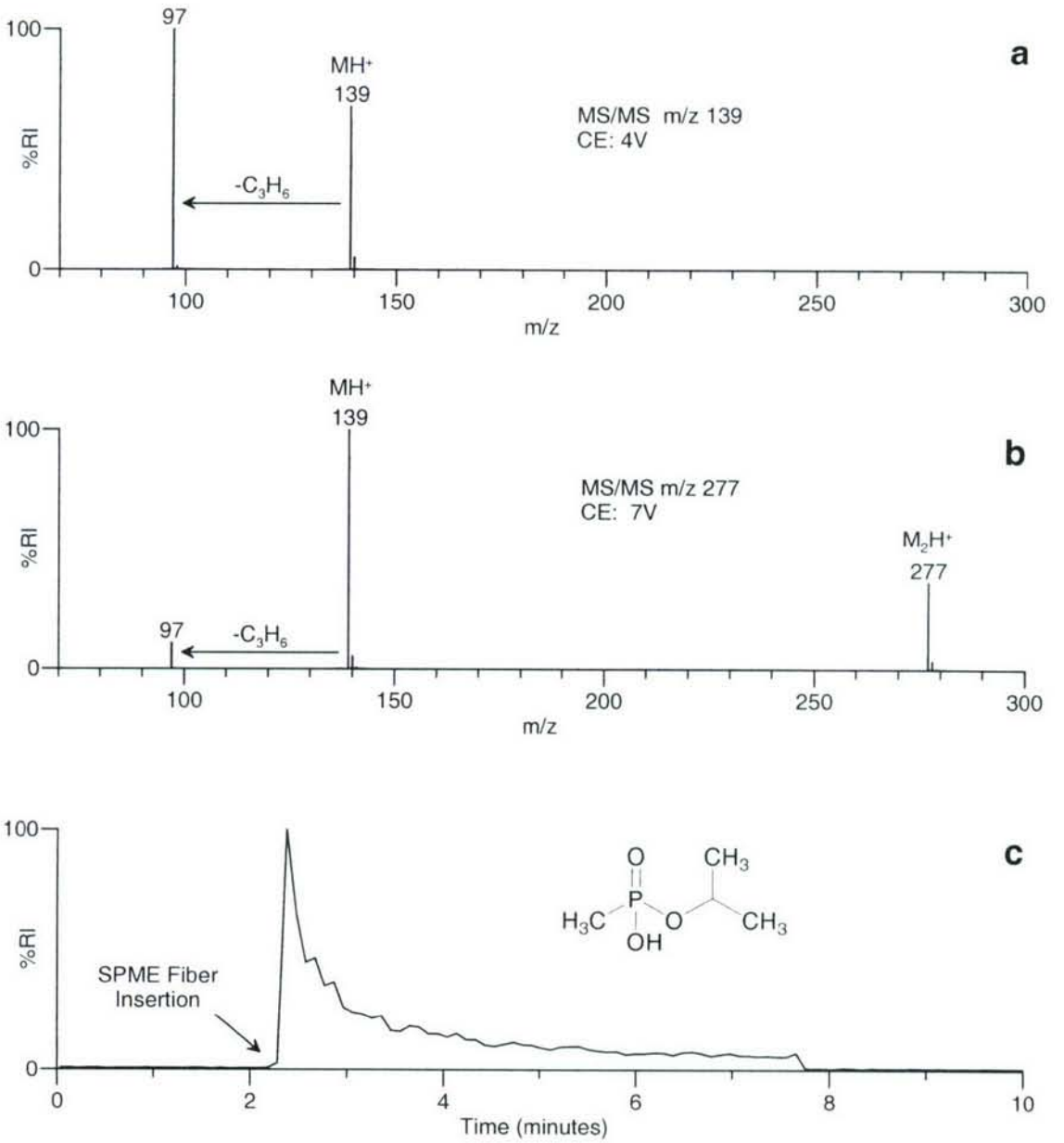

Figure 18. *Product ion mass spectra acquired for a) isopropyl methylphosphonic acid and b) its dimer acquired during c) DESI-MS (total-ion-current: m/z 70 to 700) analysis of a SPME fiber used to sample the headspace (10 min at 40 °C) above 10 µg of isopropyl methylphosphonic acid.*

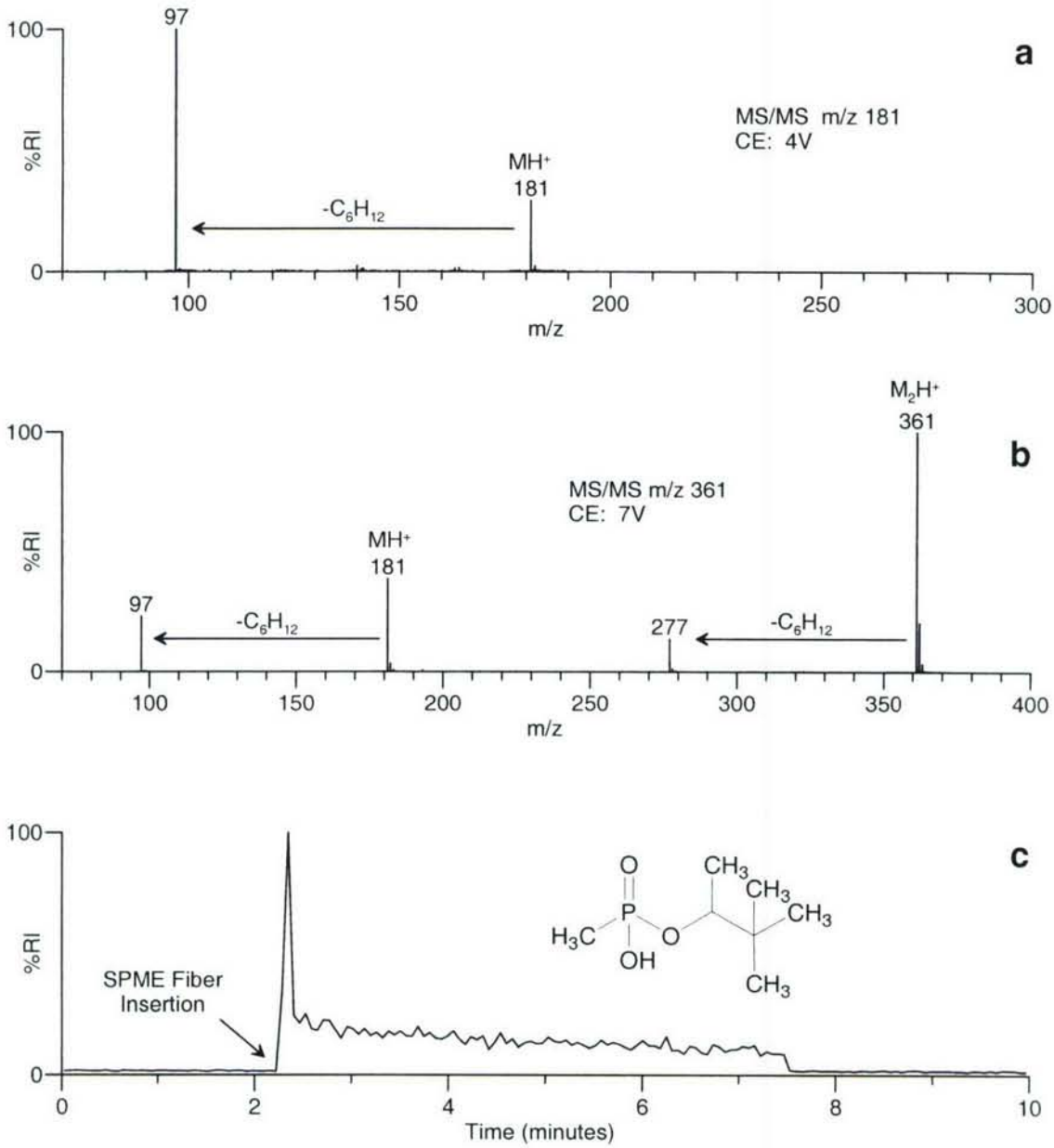

Figure 19. *Product ion mass spectra acquired for a) pinacolyl methylphosphonic acid and b)its dimer acquired during c) DESI-MS (total-ion-current: m/z 70 to 700) analysis of a SPME fiber used to sample the headspace (10 min at 80 °C) above 10 µg of pinacolyl methylphosphonic acid.*

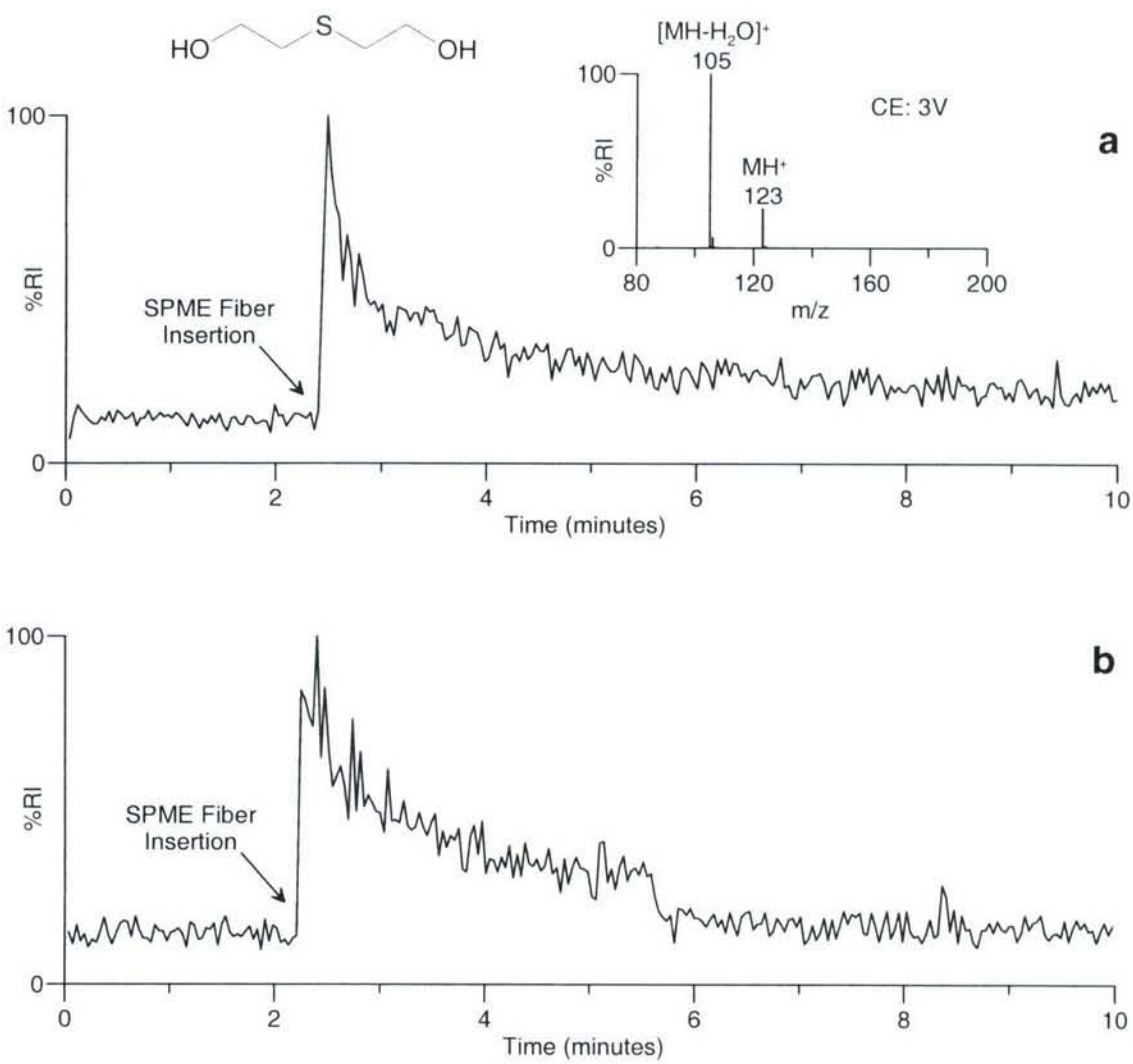

Figure 20. *DESI-MS/MS chromatograms for m/z 123 obtained during analysis of a) a SPME fiber used to sample the headspace (10 min at 80 °C) above 5 µg of thiodiglycol and b) a SPME fiber used to sample the headspace (10 min at 80 °C) above canola oil spiked at the 20 µg/g level with thiodiglycol. Inset: typical product ion mass spectrum for thiodiglycol.*

Ionization mechanisms

Several ionization mechanisms have been proposed by Cooks et al (55, 64) to account for the ions observed during DESI-MS and DESI-MS/MS and one or more mechanism may be taking place during analysis. The organophosphorus chemical warfare agents and their hydrolysis products ionize under ESI conditions and a process similar to the ESI mechanism has been proposed for DESI. It has been postulated (64) that this droplet pickup mechanism involves impact of the electrosprayed solvent droplets on the SPME fiber surface, desorption of the analyte into the solvent droplet and ionization of the analyte as the droplet evaporates, resulting in ESI like ions. This mechanism probably plays a significant role in the acquisition of DESI mass spectra of organophosphorus chemical warfare agents as the mass spectrometric

data acquired during DESI-MS (or DESI-MS/MS) experiments were indistinguishable from ESI-MS (or ESI-MS/MS) data and included the presence of sodium and acetronitrile adducts observed during ESI-MS analyses.

However several compounds, including H, do not ionize under ESI conditions (LC-ESI-MS or flow injection) and yet formed ions during DESI experiments. It is possible that these compounds are being ionized during DESI-MS by an atmospheric chemical ionization mechanism where ionization results from gas phase proton transfer to a neutral analyte that has evaporated from the SPME surface (64). If this were the case then it would be possible to protonate analytes, including H, based on the ability of the analyte to accept a proton from a donor of lesser proton affinity (64). The DESI-MS/MS (and DESI-MS) data acquired for H (Figure 15) were consistent with this mechanism.

No attempt has been made to identify the donor ion generated during electrospray ionization of the LC mobile phase. However, at some point an analyte will not be sufficiently basic to ionize by this approach. Two additional compounds that don't form ions during LC-ESI-MS also exhibited DESI-MS data. The headspace above 1,4-thioxane and toluene (Figure 21) were sampled onto a SPME fiber and protontated adducts (and a product ion for 1,4-thioxane) were observed. The analysis of hexane in a similar manner was also attempted but no signal was recorded during DESI-MS analysis, suggesting that hexane was not basic enough to accept a proton (Figure 21 a)).

It was also noted after removal of a highly exposed SPME fiber that the signal for an analyte (e.g., TEP) remained for some time. In this case the vaporized TEP could be ionizing by either an ESI like mechanism where the surface is now a gas or by the atmospheric pressure chemical ionization mechanism. The possibility of both mechanisms occurring during DESI-MS analyses cannot be ruled out.

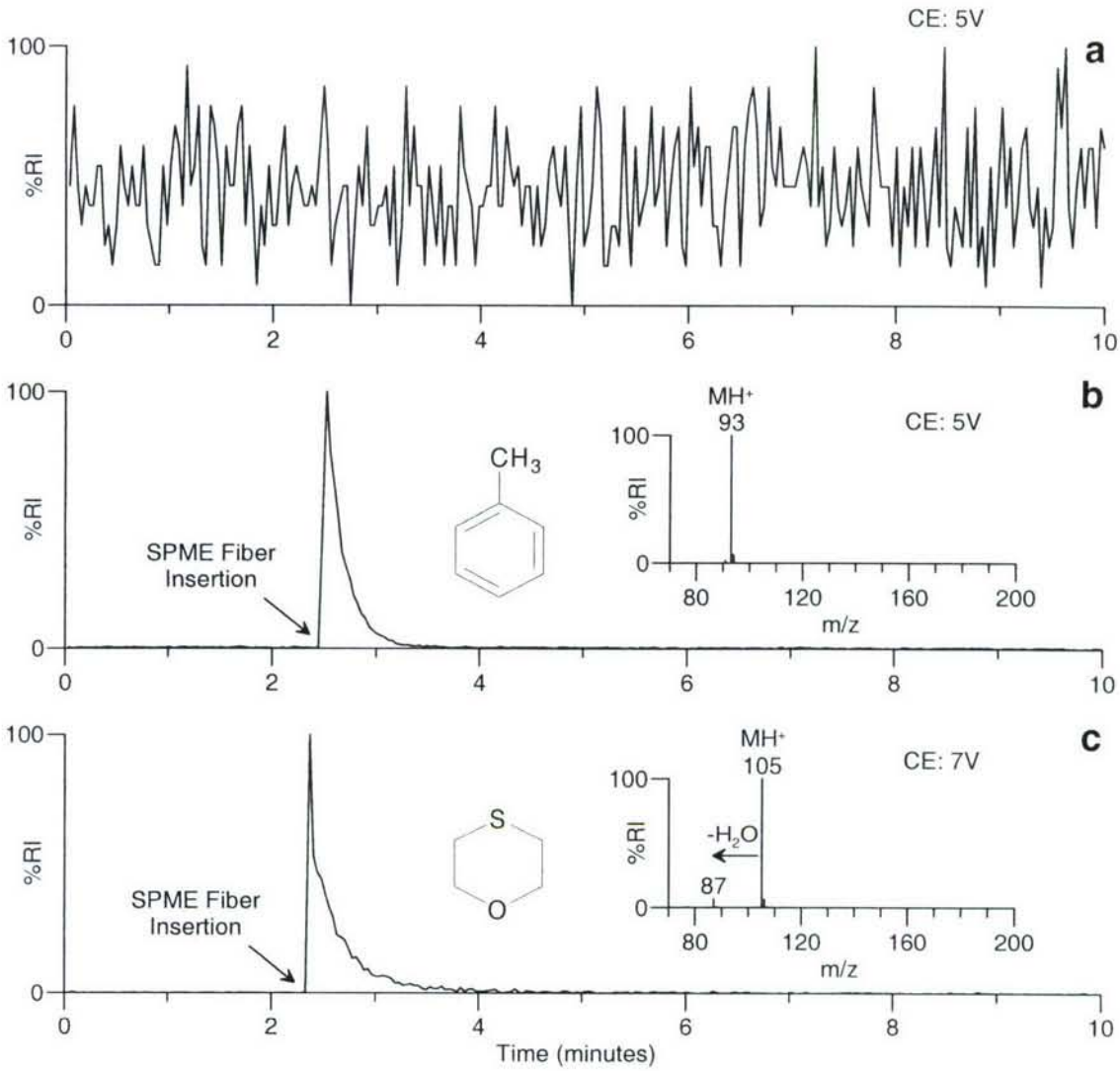

Figure 21. *DESI-MS/MS chromatogram for a) m/z 87 obtained during analysis of a SPME fiber used to sample the headspace (10 s at ambient temperature) above 1 mg of hexane, b) m/z 93 obtained during analysis of a SPME fiber used to sample the headspace (10 s at ambient temperature) above 1 mg of toluene and c) m/z 105 obtained during analysis of a SPME fiber used to sample the headspace (10 min at 30 °C) above 10 µg of 1,4-thioxane. Inset: typical product ion mass spectrum for toluene and 1,4-thioxane.*

Conclusions

Liquid chromatography electrospray ionization mass spectrometry (LC-ESI-MS) and desorption electrospray ionization mass spectrometry (DESI-MS), two techniques that have been used at DRDC Suffield (National Laboratory for CW Agent Identification) for the identification of chemical warfare agents in spiked samples, were evaluated for the determination of chemical warfare agents in spiked consumer products. Three consumer products, bottled water, canola oil and corn meal, were selected as candidates for the evaluation and comparative purposes. Each of these media was contaminated with low μg/g levels of chemical warfare agents, levels typically used for evaluation purposes by the Organisation for the Prohibition of Chemical Weapons (OPCW). LC-ESI-MS and LC-ESI-MS/MS methods, developed for the detection of these compounds in aqueous samples and extracts at DRDC Suffield, were used to successfully identify the chemical warfare agents spiked into bottled water samples.

The headspace above spiked corn meal and canola oil samples were sampled with polydimethylsiloxane/divinyl benzene (PDMS/DVB) SPME fibers. Direct analysis of SPME fibers exposed to the headspace above spiked corn meal and canola oil samples by DESI-MS and DESI-MS/MS resulted in the identification of many of the spiked compounds with higher sample throughput and less sample handling than was typically required for LC-ESI-MS/MS analysis. MS data used for the identification of all the spiked compounds were acquired in the continuum mode with a resolution of 8000, which typically resulted in mass measurement errors of 0.002 Da or less.

Three compounds, including mustard, that do not ionize during LC-ESI-MS, were protonated during DESI-MS analysis of SPME fiber samples, extending the range of compounds that may be identified with this novel technique. A mechanism based on atmospheric pressure chemical ionization of volatilized neutral analytes was consistent with the DESI-MS findings in this study. One compound, hexane, did not ionize under DESI-MS which would suggest that this compound was not sufficiently basic to accept a proton from the donor ion.

Application of the developed sample handling and analysis methodologies is anticipated during future forensic or other investigations where evidence of chemical warfare agent use is required for criminal prosecution or to insure the safety of consumer products.

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Terrorist use of chemical warfare agents could involve contamination of consumer products with chemical warfare agents or other toxic chemicals. Liquid chromatography electrospray ionization mass spectrometry (LC-ESI-MS) and desorption electrospray ionization mass spectrometry (DESI-MS) have been used at DRDC Suffield for the identification of chemical warfare agents and both approaches were evaluated for the determination of chemical warfare agents in spiked consumer products. Three consumer products, bottled water, canola oil and corn meal, were selected as candidates for the evaluation and comparative purposes. Each of these media was contaminated with low µg/g levels of chemical warfare agents, levels typically used for evaluation purposes by the Organisation for the Prohibition of Chemical Weapons (OPCW). In house LC-ESI-MS and LC-ESI-MS/MS methods were evaluated for the determination of chemical warfare agents in spiked bottled water samples. The headspaces above spiked corn meal and canola oil samples were sampled with SPME fibers and the fibers were analysed by DESI-MS and DESI-MS/MS. MS data for all the spiked compounds were acquired in the continuum mode with a resolution of 8000, which typically resulted in mass measurement errors of 0.002 Da or less. Application of the developed sample handling and analysis methodologies is anticipated during forensic or other investigations where consumer products have been deliberately contaminated with chemical warfare agents.

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Electrospray ionization
Mass spectrometry
Desorption electrospray ionization
Chemical warfare agents
Consumer products
Canola oil
Corn meal
Bottled water

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